METHOD FOR THE DETERMINATION

OF VOLATILE PETROLEUM HYDROCARBONS (VPH)

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MASSACHUSETTS DEPARTMENT OF ENVIRONMENTAL PROTECTION

1.0 SCOPE & APPLICATION

1.1 This method is designed to measure the collective concentrations of volatile aliphatic and aromatic petroleum hydrocarbons in water and soil/sediment matrices. Volatile aliphatic hydrocarbons are collectively quantitated within two ranges: C_5 through C_8 and C_9 through C_{12}. Volatile aromatic hydrocarbons are collectively quantitated within the C_9 to C_{10} range. These aliphatic and aromatic hydrocarbon ranges correspond to a boiling point range between approximately 36°C and 220°C.

1.2 This method is based on a purge-and-trap, gas chromatography (GC) procedure using a Photoionization and Flame Ionization Detector (PID/FID) in-series. This method should be used by, or under the supervision of, analysts experienced in the use of purge-and-trap systems and gas chromatographs. The analysts should be skilled in the interpretation of gas chromatograms and their use as a quantitative tool.

1.3 This method is designed to complement and support the toxicological approach developed by the Massachusetts Department of Environmental Protection to evaluate human health hazards that may result from exposure to petroleum hydrocarbons (MADEP, 1994 and MADEP, 2003). It is intended to generate data in a format suitable for evaluation by that approach, and generate data that may be compared to reporting and cleanup standards promulgated in the Massachusetts Contingency Plan (310 CMR 40.0000).

1.4 This method is also able to measure the individual concentrations of the Target VPH Analytes benzene, toluene, ethylbenzene, xylenes (BTEX), naphthalene, and methyl-tert-butylether (MTBE) in water and soil/sediment matrices. Use of this method to identify and quantify these Target Analytes is optional.

1.5 Petroleum products suitable for evaluation by this method include gasoline, mineral spirits, and certain petroleum naphthas. This method, in and of itself, is not suitable for the evaluation of kerosene, jet fuel, heating oils, lubricating oils, and/or other petroleum products which contain a significant percentage of hydrocarbons heavier than C_{12}.

1.6 The Reporting Limit (RL) of this method for each of the collective aliphatic and aromatic fractional ranges is approximately 5-10 mg/kg in soil/sediment and approximately 100-150 µg/L in water. The RL of this method for Target Analytes is compound-specific, and ranges from approximately 0.050 to 0.25 mg/kg in soil/sediment, and 1 to 5 µg/L in water.

1.7 This method includes a series of data adjustment steps to determine the concentrations of the aliphatic and aromatic ranges of interest. These steps may be taken by the laboratory or by the data user.

1.8 Data reports generated using this method must contain all of the information in the form provided in Appendix 3. The format of these reports is left up to the individual laboratories. However, the format of the Laboratory Certification must follow the format presented in Appendix 3.

1.9 Like all GC procedures, this method is subject to a "false positive" bias in the reporting of Target VPH Analytes, in that non-targeted hydrocarbon compounds eluting or co-eluting within a specified retention time window may be falsely identified and/or quantified as a Target VPH Analyte. Confirmatory analysis by a GC/mass spectrometry (MS) procedure or other suitable method is recommended in cases where a Target VPH Analyte reported by this method exceeds an applicable reporting or cleanup standard, and/or where co-elution of a non-targeted hydrocarbon compound is suspected.

1.10 The first draft of this method was evaluated by two inter-laboratory "Round Robin" testing programs. In the final evaluation effort, participating laboratories were provided (single-blind) sand samples spiked with gasoline, and a "real world" groundwater sample contaminated by gasoline. Laboratory proficiency was evaluated using a Z-score approach. Data received from 21 laboratories performing this method without significant modifications are summarized below:

Matrix	# Labs Proficient	% Labs Proficient	Data from Proficient Laboratories		
			Fraction	%RSD	% labs within +/- 30% mean value
soil	20	95	C_5-C_8 Aliphatics	28	80
			C_9-C_{12} Aliphatics	52	50
			Total GC/FID	31	70
			C_9-C_{10} Aromatics	24	80
water	17	81	C_5-C_8 Aliphatics	31	71
			C_9-C_{12} Aliphatics	44	47
			Total GC/FID	24	76
			C_9-C_{10} Aromatics	20	82

Laboratory and method performance were believed to have been adversely impacted by the use of multiple chromatographic columns, which may have significantly altered the placement of aliphatic hydrocarbons into either the C_5 - C_8 or C_9 - C_{12} Aliphatic Hydrocarbon fractions. Better performance was noted for the aromatic fraction and Total GC/FID data. Improvements incorporated into this final method are expected to significantly improve overall method performance.

1.11 This method is one way to quantify collective concentrations of volatile aliphatic and aromatic petroleum hydrocarbons within specified carbon-number-ranges. It has been designed in a manner that attempts to strike a reasonable balance between analytical method performance and utility. In this manner, assumptions and biases have been structured into the method to help ensure protective, though not overly conservative data.

As an example, the Department recognizes that branched alkanes have lower boiling points than their n-alkane counterpart, while many of the cycloalkane constituents of gasoline range volatile organics have higher boiling points than their n-alkane counterpart. As a consequence:

(1) Depending upon the specific chromatographic column used, most branched C_9 alkanes are expected to elute before n-nonane, the beginning marker compound for the C_9 through C_{12} aliphatic hydrocarbon range, and will be conservatively counted in the more toxic C_5 through C_8 aliphatic hydrocarbon range;

(2) Depending upon the specific chromatographic column used, most branched C_5 alkanes will elute before n-pentane, the beginning marker compound for the C_5 through C_8 aliphatic hydrocarbon range, and will not be counted at all in the C_5 through C_8 aliphatic hydrocarbon range; and

(3) Depending upon the specific chromatographic column used, most cycloalkanes within the C_5 through C_8 and C_9 through C_{12} aliphatic hydrocarbon ranges will be counted within their proper range with the exception of some C_{12} cycloalkanes which will elute after naphthalene, the end marker compound for the C_9 through C_{12} aliphatic hydrocarbon range.

Based on the nature of petroleum releases encountered in the environment, the collective concentrations of the volatile aliphatic ranges as measured by the VPH Method are considered to be suitable for the evaluation of the risks posed by these releases, consistent with the toxicological approach developed by the Department to evaluate human health hazards that may result from exposure to petroleum hydrocarbons (MADEP, 1994 and MADEP, 2003).

1.12 There may be better, more accurate, and/or less conservative ways to produce VPH target and range data. MADEP encourages methodological innovations that (a) better achieve method and/or data quality objectives, (b) increase analytical precision and accuracy, (c) reduce analytical uncertainties and expenses, and/or (d) reduce the use of toxic solvents and generation of hazardous wastes. For

example, GC/MS has shown promise as an alternative analytical system to produce both acceptable range and target VPH data.

All significant modifications to this method, however, must be disclosed and described on the data report form, as detailed in Section 11.3 and the MADEP MCP Analytical Method Report Certification Form (See Appendix 3, Exhibit 2, Question D). Laboratories who make such modifications, and or develop and utilize alternative approaches and methods, are further required to demonstrate:

- That such modifications or methodologies adequately quantify the petroleum hydrocarbon target ranges, as defined in Sections 3.4 through 3.6 of this document, ensuring that any methodological uncertainties or biases are addressed in a manner that ensures protective (i.e., conservative) results and data (e.g., over, not under-quantification of the more toxic ranges);

- That such modifications and/or methodologies employ and document initial and continuing Quality Assurance/ Quality Control procedures consistent with similar approaches detailed in the MADEP Compendium of Analytical Methods; and

- That such methods and procedures are fully documented in a detailed Standard Operating Procedure.

1.13 Additional information and details on the MADEP VPH/EPH approach, and on the results of inter-laboratory "Round Robin" evaluations of this method, are available on the World Wide Web at http://www.magnet.state.ma.us/dep/bwsc/pubs.htm.

1.14 This method is intended to be used in conjunction with the current version of CAM IV A, "Quality Assurance and Quality Control Requirements for the Method For The Determination of Volatile Petroleum Hydrocarbons (VPH)". CAM IV A was developed by the Department to complement the MADEP VPH Method and to provide more detailed guidance regarding compliance with the quality control requirements and performance standards of the VPH Method.

2.0 SUMMARY OF METHOD

2.1 Samples are analyzed using purge-and-trap sample concentration. The gas chromatograph is temperature programmed to facilitate separation of organic compounds. Detection is achieved by a photoionization detector (PID) and flame ionization detector (FID) in series. Quantitation is based on comparing the PID and FID response of a sample to a standard comprised of aromatic and aliphatic hydrocarbons. The PID chromatogram is used to determine the individual concentrations of Target Analytes (BTEX/MTBE/naphthalene) and collective concentration of aromatic hydrocarbons within the C_9 through C_{10} range. The FID chromatogram is used to determine the collective concentration of aliphatic hydrocarbons within the C_5 through C_8 and C_9 through C_{12} ranges.

2.2 This method is suitable for the analysis of waters, soils, sediments, wastes, sludges, and non-aqueous phase liquid (NAPL) samples. However, it should be noted that the method was validated only for soil and water matrices. Water samples may be analyzed directly for volatile petroleum hydrocarbons by purge-and-trap concentration and gas chromatography. Soil/sediment samples are dispersed in methanol to dissolve the volatile organic constituents. An aliquot of the methanol extract is then analyzed by purge-and-trap GC.

2.3 This method is based on (1) USEPA Methods 5030B, 5035A, 8000B, 8021B, and 8015B, SW-846, "Test Methods for Evaluating Solid Wastes", (2) Draft "Method for Determination of Gasoline Range Organics", EPA UST Workgroup, November, 1990; and (3) "Modified GRO Method for Determining Gasoline Range Organics ", Wisconsin Department of Natural Resources, PUBL-SW-140, 1992.

3.0 DEFINITIONS

3.1 **Analytical Batch** is defined as a group of field samples with similar matrices which are processed as a unit. For Quality Control purposes, if the number of samples in such a group is greater than 20, then each group of 20 samples or less is defined as a separate analytical batch.

3.2 **Calibration Standards** are defined as a series of standard solutions prepared from dilutions of a stock standard solution, containing known concentrations of each analyte and surrogate compound of interest.

3.3 **Continuing Calibration Standard** is defined as a calibration standard used to periodically check the calibration state of an instrument. The continuing calibration standard is prepared from the same stock solution as calibration standards, and is generally one of the mid-level range calibration standard dilutions.

3.4 **C_5 through C_8 Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds which contain between five and eight carbon atoms and are associated with the release of a petroleum product to the environment. In the VPH method, C_5 through C_8 aliphatic hydrocarbons are defined and quantitated as compounds which elute from n-pentane (C_5) to just before n-nonane (C_9).

3.5 **C_9 through C_{12} Aliphatic Hydrocarbons** are defined as all aliphatic hydrocarbon compounds which contain between nine and 12 carbon atoms and are associated with the release of a petroleum product to the environment. In the VPH method, C_9 through C_{12} aliphatic hydrocarbons are defined and quantitated as compounds which elute from n-nonane (C_9) to just before naphthalene.

3.6 **C_9 through C_{10} Aromatic Hydrocarbons** are defined as all aromatic hydrocarbon compounds which contain between nine and 10 carbon atoms and are associated with the release of a petroleum product to the environment. In the VPH method, C_9 through C_{10} aromatic hydrocarbons are defined and quantitated as compounds which elute from just after o-xylene to just before naphthalene; therefore this range will include any unsaturated hydrocarbons (e.g., alkenes, alkynes, carbonyls, ethers, etc.). Although naphthalene is an aromatic compound with 10 carbon atoms, it is excluded from this range because it is evaluated as a separate (Target) analyte.

3.7 **Field Duplicates** are defined as two separate samples collected at the same time and place under identical circumstances and managed the same throughout field and laboratory procedures. Analyses of field duplicates give a measure of the precision associated with sample collection, preservation, and storage, as well as laboratory procedures.

3.8 **Laboratory Control Sample (LCS)** is defined as a reagent water blank (when associated with aqueous samples) or clean methanol blank (when associated with soil/sediment samples) fortified with a matrix spiking solution. The LCS is prepared and analyzed in the same manner as a sample and its purpose is to determine the bias of the analytical method.

3.9 **Laboratory Control Sample Duplicate (LCSD)** is defined as a reagent water blank (when associated with aqueous samples) or clean methanol blank (when associated with soil/sediment samples) fortified with a matrix spiking solution. The LCSD is prepared separately from the LCS but is prepared and analyzed in the same manner as the LCS. The analysis of LCS duplicates provides a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.10 **Laboratory Method Blank (LMB)** is defined as an aliquot of reagent water (when associated with aqueous samples) or clean methanol (when associated with soil/sediment samples) spiked with a surrogate standard. The laboratory method blank is prepared and analyzed in the same manner as a sample, exposed to all glassware, solvents, reagents, and equipment. A laboratory method blank is analyzed with every batch of samples, to determine if method analytes or other interferences are present in the laboratory environment, reagents, or equipment.

3.11 **Matrix Duplicates** are defined as split samples prepared and analyzed separately with identical procedures. For soil/sediment samples, matrix duplicate samples are taken from the same sampling container. For aqueous samples, a separate container is used for the matrix duplicate sample. The analysis of matrix duplicates gives a measure of the precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.12 **Matrix Spike (MS) Sample** is defined as an environmental sample which has been spiked with a matrix spiking solution containing known concentrations of method analytes. The purpose of the MS sample is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined through the separate analyses of an unspiked sample aliquot. The measured values in the MS sample must be corrected for background concentrations when calculating recoveries of spiked analytes.

3.13 **Matrix Spiking Solution** is defined as a solution prepared from a separate source than used for the calibration standards, containing known concentrations of method analytes.

3.14 **System Solvent Blank (SSB)** is defined as an aliquot of organic-free water (ASTM Type I reagent grade) and purge-and-trap grade, or equivalent, methanol. For water samples 4.0 uL of methanol is mixed with 5.0 mL of water and for soil samples 100 uL of methanol is mixed with 4.9 mL of water. The SSB is analyzed in the same manner as a sample, exposed to all glassware, solvents, reagents, and equipment. Surrogates must not be spiked into SSBs. An SSB provides one way of determining the level of noise and baseline rise attributable solely to the analytical system, in the absence of any other analytes or non-analytical related contaminants.

3.15 **Target VPH Analytes** are defined as benzene, toluene, ethylbenzene, m-xylene, p-xylene, o-xylene, naphthalene, and methyl-tert-butylether.

3.16 **Unadjusted C_5 through C_8 Aliphatic Hydrocarbons** are defined as all petroleum hydrocarbon compounds which elute on the FID chromatogram from n-pentane (C_5) to just before n-nonane (C_9).

3.17 **Unadjusted C_9 through C_{12} Aliphatic Hydrocarbons** are defined as all petroleum hydrocarbon compounds which elute on the FID chromatogram from n-nonane (C_9) to just before naphthalene.

3.18 **Volatile Petroleum Hydrocarbons (VPH)** are defined as collective fractions of hydrocarbon compounds eluting from n-pentane to naphthalene, excluding Target VPH Analytes. VPH is comprised of C_5 through C_8 Aliphatic Hydrocarbons, C_9 through C_{12} Aliphatic Hydrocarbons, and C_9 through C_{10} Aromatic Hydrocarbons.

3.19 **Volatile Petroleum Hydrocarbon (VPH) Component Standard** is defined as a 15 component mixture of the aliphatic and aromatic compounds and one surrogate listed in Table 1. The compounds comprising the VPH Component Standard are used to (a) define the individual retention times and chromatographic response factors for each of the Target VPH Analytes, (b) define and establish the windows for the collective aliphatic and aromatic hydrocarbon ranges of interest, and (c) determine average calibration factors or generate calibration curves that can in turn be used to calculate the collective concentration of hydrocarbons within these ranges.

3.20 All other terms are as defined in the most current version of SW-846, "Test Method for Evaluating Solid Waste", USEPA.

Table 1. Volatile Petroleum Hydrocarbon (VPH) Component Standard

Compound	Retention Time (minutes)[1]		MDL[2]			
	PID	FID	Water (µg/L)		Soil (µg/g)	
			PID	FID	PID	FID
n-Pentane	N/A	7.00		1.1		0.28
2-Methylpentane	N/A	8.65		2.2		0.47
Methyl-tert-butylether	9.18	9.18	0.47		0.39	
2,2,4-Trimethylpentane	N/A	13.42		1.5		0.22
Benzene	14.25	14.25	0.21		0.14	
Toluene	20.11	20.11	0.55		0.42	
n-Nonane	N/A	24.11		0.44		0.25
n-Decane	N/A	TBD		TBD		TBD
Ethylbenzene	24.46	24.46	0.16		0.16	
m- & p- Xylene	24.66	24.66	0.62		0.51	
o-Xylene	25.75	25.75	0.81		0.28	
1,2,4-Trimethylbenzene	28.64	28.64	0.34		0.25	
n-Butylcyclohexane	N/A	TBD		TBD		TBD
Naphthalene	33.05	33.05	1.57		0.15	
2,5-Dibromotoluene (surrogate)	35.21	35.21			0.68	

[1]Results obtained using an RTX-502.2 column and chromatographic conditions described in Sections 6.3 and 9.2, respectively
[2] Single laboratory MDL study; see Appendix 1 for more details
TBD = To Be Determined

4.0 INTERFERENCES

4.1 Samples can become contaminated by diffusion of volatile organics through the sample container septum during shipment and storage or by dissolution of volatiles into the methanol used for preservation. Trip blanks prepared from both reagent water (when associated with aqueous samples) and methanol (when associated with soil/sediment samples) should be carried through sampling and subsequent storage and handling to serve as a check on such contamination.

4.2 Cross-contamination can occur whenever a low-concentration sample is analyzed immediately after a high-concentration sample. To reduce carryover, the sample syringe and/or purging device must be rinsed between samples with reagent water or solvent. For volatile samples containing high concentrations of water-soluble materials, suspended solids, high boiling-point compounds or organohalides, it may be necessary to wash the syringe or purging device with a detergent solution, rinse with distilled water, and then dry in an oven at 105°C between analyses. The trap and other parts of the system are also subject to contamination; therefore, frequent bake-out and purging of the entire system may be required. A screening step is recommended to protect analytical instrumentation. Whenever an unusually concentrated sample is encountered, it must be followed by

the analysis of a system solvent blank or laboratory method blank to check for cross-contamination. However, due to the potential for samples to be analyzed using an autosampler, the ability to perform this blank analysis may not always be possible. If the sample analyzed immediately after the unusually concentrated sample is free from contamination, then the assumption can be made that carryover or cross-contamination is not an issue. However, if this sample did detect analytes which were present in the unusually concentrated sample, reanalysis is required for all samples analyzed after this highly concentrated sample which detected similar analytes.

4.3 The response selectivity of a photoionization detector (PID) is used in this method to differentiate aromatic hydrocarbons from aliphatic hydrocarbons. All compounds eluting on the PID chromatogram after o-xylene are identified by the method as aromatic hydrocarbons. This will lead to an overestimation of aromatic hydrocarbons within samples, as certain aliphatic compounds will elicit a response on the PID, particularly unsaturated compounds such as alkenes. The significance and implications of this overestimation will vary from sample to sample; where less conservative data are desired, additional actions should be considered to minimize the detection of non-aromatic compounds, including the use of a lower energy PID lamp and/or an alternative chromatographic column

5.0 HEALTH AND SAFETY ISSUES

The toxicity and carcinogenicity of each reagent used in this method have not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis.

6.0 APPARATUS AND MATERIALS

6.1 The following glassware is used in this method:

6.1.1 VOC Vials: Wide mouth 60-mL VOC vials or 40-mL VOC vials with Teflon/silicone septa for soil/sediment; 40-mL VOC vials with Teflon/silicone septa for waters.

6.1.2 Class “A” Volumetric flasks: 10-mL, 50-mL, 100-mL, and 1,000-mL with a ground-glass stopper.

6.2 Analytical balance: An analytical balance capable of accurately weighing 0.0001 g must be used for weighing standards. A top-loading balance capable of weighing to the nearest 0.1 g must be used for weighing soil/sediment samples.

6.3 **Gas Chromatography**

6.3.1 Gas Chromatograph: An analytical system complete with temperature programmable gas chromatograph and purge-and-trap concentrator. The data station must be capable of storing and reintegrating chromatographic data and must be capable of determining peak areas using a forced baseline projection.

6.3.2 Chromatographic Column: The required column is: 105 m x 0.53 mm I.D. Restek RTX-502.2 with 3 micron film thickness, or column with equivalent chromatographic properties.

NOTE: Based upon data obtained from the Round Robin testing programs, the choice of chromatographic column may have a significant impact on the apportionment and quantitation of aliphatic and aromatic compounds within the fractional ranges specified in this method. Substitution of the required column is allowed, only if it can be demonstrated that the selected column has equivalent chromatographic properties and retention times for the aliphatic and aromatic compounds and ranges of interest.

To demonstrate equivalency of column chromatography, a neat gasoline standard must be analyzed on both the required column and the proposed substitute column,

with all other run and system parameters held constant. The concentrations of C_5 - C_8 and C_9 - C_{12} Aliphatic Hydrocarbons must be determined for each column (in which the concentration of the Target/aromatic analytes have been subtracted from the GC/FID response). The Relative Percent Difference between the concentrations of each fraction obtained for each column must be equal to or less than 25%.

6.3.3 Detectors: The method requires the use of a Photoionization Detector (PID) in series with a Flame Ionization Detector (FID); the PID first in the series. The method is based upon the use of a 10.0 +/- eV PID lamp, although lower energy lamps are permissible in order to minimize PID response to aliphatic compounds. In lieu of an in-series arrangement, in-parallel PID and FID units may be also used if the reporting limit for the method is not adversely effected.

6.3.4 Purge-and-trap (P&T) system: The purge-and-trap system consists of a sample purging chamber, a concentrating trap, and a thermal desorber. Complete systems are available commercially.

6.3.4.1 The purging chamber must be designed to accept 5 mL samples with a water column at least 3 cm deep. Purging devices larger than 5 mL have a reduced purging efficiency and should not be used. The gaseous headspace between the water column and the top of the vessel should be at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. Fritted glass or needle sparge cells may be used. If needle sparge cells are used, the purge gas must be introduced no more than 5 mm from the base of the water column. Alternate sample purging devices may be used, provided an equivalent performance is demonstrated.

6.3.4.2 The recommended trap should be at least 25 cm long and have an inside diameter of at least 0.105 inches. The trap should be packed with 400 mg of Carbopack B (Supelco Cat. No. 2-0273). Alternative trap packing materials include: Tenax GC (or equivalent); 7.6 cm Carbopack B and 1.3 cm Carbosieve S-III (Supelco Cat No. 2-0321); 7.7 cm Carbopack C and 1.2 cm Carbopack B (Supelco Cat No. 2-1064); or equal volumes of Tenax, silica gel, and charcoal as described in EPA SW-846 Method 5030B. In general, Carbopack trap packing materials are recommended because they have less of a tendency to retain methanol, which could interfere with the elution of pentane and quench the FID flame. The recommended trap length and packing materials may be varied as long as equivalent performance (i.e., meeting QC criteria of method) has been verified.

6.3.4.3 Prior to initial use, the Carbopack B trap should be conditioned overnight at 270°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to a hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min. at 260°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples. Devices other than the traps recommended in Section 6.3.4.2 should be conditioned and desorbed according to the manufacturer's guidelines.

6.3.4.4 The desorber should be capable of rapidly heating the trap to 260°C.

6.4 Ultrasonic bath.

6.5 Disposable pipets: Pasteur.

6.6 Syringes: 5-mL Luerlock glass hypodermic and 5-mL gas-tight syringe with shutoff valve.

6.7 Syringe valve: Two-way, with luer-lock connections.

6.8 Microsyringes: 1-µL, 5-µL, 10-µL, 25-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL.

6.9 Spatula: Stainless steel.

6.10 Drying oven.

6.11 Dessicator.

7.0 REAGENTS AND STANDARDS

7.1 **Reagents**

7.1.1 Reagent Water: organic-free water (ASTM Type I reagent grade water).

7.1.2 Solvent: methanol; purge-and-trap grade or equivalent. Store away from other solvents.

7.2 **Stock Standard Solution**

Prepare stock standard solutions in methanol at approximately 10 micrograms per microliter (µg/µL), or purchase certified solutions. Preparation of stock standards and component standards should be done using volumetric glassware.

7.2.1 The stock standard solution consists of the 15 VPH component standards listed in Table 1 and a surrogate standard. Prepare the stock standard solution by accurately weighing approximately 0.1000 g of each VPH Component Standard (listed in Table 2) and the surrogate standard. Dissolve each compound in methanol and dilute to volume in a 10-mL volumetric flask.

7.2.1.1 Place about 8 mL of methanol in a 10-mL tared ground-glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 min. or until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

7.2.1.2 Using a 500-µL syringe, immediately add the required volume of each VPH Component Standard and surrogate to the flask, then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

7.2.1.3 Dilute to volume, stopper, and then mix by inverting the flask three times. Calculate the concentration in µg/µL from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard, provided such purities are certified by the manufacturer or by an independent source.

7.2.1.4 Transfer the stock standard solution into a Teflon-lined screw-cap or crimp cap bottle. Store, with minimal headspace, at -10°C to -20°C and protect from light.

7.2.2 A separate stock standard solution containing only the surrogate must be prepared. Prepare and store this solution using the procedure listed in Section 7.2.1.

7.2.3 Stock standard solutions must be replaced after 6 months, or sooner if comparison with check standards indicates a problem.

7.3 **Primary Dilution Standard**

Using the stock standard solutions, prepare primary dilution standards in methanol, as needed. The primary dilution standards should be prepared at the concentration shown in Table 2. These standards should be stored with minimal headspace, at -10°C to -20°, and should be checked frequently for signs of degradation or evaporation. The primary dilution standards should be replaced at least monthly.

Table 2. Recommended Primary Dilution Standard

Component	Concentrations, µg/mL
Pentane	100
2-Methyl pentane	100
Methyl-t-butyl ether	100
2,2,4-Trimethylpentane	100
Benzene	100
Toluene	100
n-Nonane[1]	100[1]
n-Decane	100
Ethylbenzene	100
m-Xylene	100
p-Xylene	100
o-Xylene	100
1,2,4-Trimethylbenzene	100
n-Butylcyclohexane	100
Naphthalene	100
2,5-dibromotoluene (surrogate)	100

[1] Erratic performance has been noted for n-nonane; calibration of C_9-C_{12} aliphatics with n-decane and n-butylcyclohexane only is allowed. However, n-nonane must be retained in the primary dilution standard for use as a range marker compound (see Table 6).

7.4 **VPH Calibration Standards**

Prepare VPH Calibration standards in reagent water from the primary dilution standard (in methanol) at a minimum of five concentration levels (i.e., 1x, 5x, 25x, 100x and 200x). The lowest concentration (1x) determines the minimum working range of the calibration curve and defines the Reporting Limit (RL) for individual Target Analytes. The highest concentration (200x) defines the maximum upper working range of the calibration curve. Target analytes may not be reported above this concentration without sample dilution. RLs for collective VPH aliphatic and aromatic hydrocarbon ranges are discussed in Section 12.0.

7.4.1 Rapidly inject an accurate volume of the primary dilution standard into the water in the expanded area of a filled 10-mL or 100-mL volumetric flask, depending on the calibration standard concentration. Remove the needle quickly after injection.

7.4.2 Mix aqueous standards by inverting the flask three times.

7.4.3 Discard the solution contained in the neck of the flask, and fill the sample syringe from the standard solution contained in the expanded area of the flask.

7.4.4 Do not use pipettes to dilute or transfer samples or aqueous standards.

The recommended concentrations for calibration standards are provided in Table 3. Aqueous standards are not stable and should be discarded after one hour.

7.5 **Surrogate Standard**

The analyst must monitor both the performance of the analytical system and the effectiveness of the method in dealing with sample matrices by spiking each sample, blank, LCS, LCSD, and matrix spike with a surrogate standard. The surrogate standard is included in the VPH calibration standard solutions. The recommended surrogate standard is 2,5-dibromotoluene, which elutes after all aliphatic and aromatic compounds of interest. However, other surrogates may be used as long as they are adequately resolved from the components of interest.

7.5.1 Surrogate Spiking Solution: From a stock standard solution prepared as in Section 7.2.2, prepare a surrogate spiking solution at 50 µg/mL in methanol. Add 4.0 µL of this surrogate spiking solution directly into the 5-mL syringe with every aqueous sample, blank, LCS, LCSD, and matrix spike. Add 1.0 mL of the surrogate spiking solution to soil/sediment samples during the extraction step (See Section 9.1.3.2). The use of higher concentrations are permissible and advisable when spiking highly contaminated samples.

7.6 **Matrix Spiking Solution**

The recommended matrix spiking solution, consisting of the full analyte list (VPH Component Standard), is prepared in methanol at a nominal concentrations of 50 µg/mL.

7.7 **Petroleum Reference Standard (To demonstrate equivalency of column chromatography)**

The Petroleum Reference Standard consists of an API or commercial gasoline standard. Prepare Petroleum Reference Standard Spiking Solutions by accurately weighing approximately 0.0100 g of neat product. Dissolve the neat product in methanol and dilute to volume in a 100-mL volumetric flask.

Table 3. Recommended VPH Calibration Standard Concentrations

Component	Nominal Concentration (µg/L)				
Pentane	1	5	25	100	200
2-Methylpentane	1	5	25	100	200
Methyl-t-butyl ether	1	5	25	100	200
2,2,4-Trimethylpentane	1	5	25	100	200
Benzene	1	5	25	100	200
Toluene	1	5	25	100	200
n-Nonane[1]	1	5	25	100	200
n-Decane	1	5	25	100	200
Ethylbenzene	1	5	25	100	200
m-Xylene	1	5	25	100	200
p-Xylene	1	5	25	100	200
o-Xylene	1	5	25	100	200
1,2,4-Trimethylbenzene	1	5	25	100	200
n-Butylcyclohexane	1	5	25	100	200
Naphthalene	1	5	25	100	200
2,5-Dibromotoluene (surrogate)	1	5	25	100	200

[1] Erratic performance has been noted for n-nonane; calibration of C_9-C_{12} aliphatics with n-decane and n-butylcyclohexane only is allowed. However, n-nonane must be retained in the calibration standard for use as a range marker compound (see Table 6).

8.1 Aqueous Samples

8.1.1 Aqueous samples should be collected in duplicate (or the number of vials directed by the laboratory) without agitation and without headspace in contaminant-free 40 mL glass VOC vials with Teflon-lined septa screw caps. The Teflon liner must contact the sample. All samples must be chemically preserved as follows:

a. Samples analyzed with ambient purge temperature: Samples must be acidified to a pH of 2.0 or less at the time of collection. This can generally be accomplished by adding 3 or 4 drops (0.1 to 0.2 mL) of 1:1 HCl (1 part reagent water and 1 part concentrated HCl) to a 40-mL sample vial. Samples must be cooled to 4°C ± 2ºC immediately after collection.

b. Samples analyzed with heated purge temperature: Samples must be treated to a pH of 11.0 or greater at the time of collection. This can be accomplished by adding 0.40 and 0.44 grams of trisodium phosphate dodecahydrate (TSP) to a 40-mL sample vial. Samples must be cooled to 4°C ± 2ºC immediately after collection.

8.1.2 A chain-of-custody form must accompany all sampling vials and must document the date and time of sample collection and preservation method used. The pH of all water samples must be determined by the laboratory after sample analysis has been completed. The pH measurement may be performed on leftover sample. Any acid-preserved sample found to contain a pH above 2 must be so noted on the laboratory/data report sheet. Any TSP-preserved sample found to contain a pH <11 must be so noted on the laboratory data report sheet.

8.1.3 A reagent water trip blank, preserved in the same manner as the samples, should accompany each batch of water samples.

8.1.4 Any sample received by the laboratory that is not packed in ice or cooled to 4°C ± 2ºC must be so noted on the laboratory/data report sheet. The temperature of the cooler must be recorded by the laboratory upon receipt.

8.1.5 Aqueous samples must be analyzed within 14 days of collection.

8.2 Soil/Sediment Samples

8.2.1 Soil/sediment samples must be collected in a manner that minimizes sample handling, environmental exposure and/or aeration. The use of specially designed air-tight collection samplers or a 30-mL plastic syringe with the end sliced off is recommended. All soil/sediment must be removed from the glass threads of the vial to ensure an adequate seal. Samples must be cooled to 4°C ± 2ºC immediately after collection.

8.2.2 **Methanol preservation of soil/sediment samples is mandatory.** Methanol (purge-and-trap grade) must be added to the sample vial before or immediately after sample collection. In lieu of the in-field preservation of samples with methanol, soil samples may be obtained in specially-designed air tight sampling devices, provided that the samples are extruded and preserved in methanol within 48 hours of collection. Additional details and recommendations on soil/sediment sampling are provided in Appendix 4.

8.2.3 The desired ratio of soil/sediment-to-methanol is 1 gram soil/sediment to 1 mL methanol/, +/- 25%. The exact weight of the soil/sediment sample and volume of methanol must be known or ascertained by the laboratory when calculating and reporting soil/sediment concentration data. A recommended practice is for a laboratory to provide labeled, pre-weighed sampling vials with the measured volume of methanol clearly indicated to the field sampling technician. The laboratory "fill line" indicating the height of the methanol meniscus should be permanently marked on the side of the sampling container. After the soil sample is added to the methanol in the sampling container, the sample "fill line" indicating the height of the sample-displaced (increased) methanol level should also be

marked by the field sampling technician. **In all cases, the soil/sediment sample in the vial must be completely covered by methanol.**

8.2.4 Samples for VPH analysis should be collected in duplicate 60-mL or 40-mL VOC vials with Teflon-lined septa screw caps. An additional sample of the soil/sediment must also be obtained (without methanol) to allow for a determination of moisture content and VPH dry weight correction factors.

8.2.5 A methanol trip blank should accompany each batch of soil/sediment samples.

8.2.6 A chain-of-custody form must accompany all sampling vials and must document the date and time of sample collection and, where appropriate, the volume of methanol added. Observations of vial leakage must be so noted on the laboratory/data report sheet.

8.2.7 Any sample received by the laboratory that is not packed in ice or cooled to 4°C ± 2ºC must be so noted on the laboratory/data report sheet. The temperature of the cooler must be recorded by the laboratory upon receipt.

8.2.8 Soil/sediment samples must be analyzed within 28 days of collection.

8.3 A summary of sample collection, preservation and holding times is provided in Table 4.

Table 4. Holding Times and Preservatives for VPH Samples

Matrix	Container	Preservation	Holding Time
Aqueous Samples (using ambient temperature purge)	40-mL VOC vials w/ Teflon-lined septa screw caps	Add 3 to 4 drops of 1:1 HCl to pH <2; cool to 4°C ± 2ºC	14 days
Aqueous Samples (using heated purge)[1]	40-mL VOC vials w/ Teflon-lined septa screw caps	Add 0.40 to 0.44 grams of trisodium phosphate dodecahydrate to pH >11; cool to 4°C ± 2ºC	14 days
Soil/Sediment Samples[2]	VOC vials w/ Teflon-lined septa screw caps. 60-mL vials: add 25 g soil/sediment 40-mL vials: add 15 g soil/sediment	1 mL methanol for every g soil/sediment; add before or at time of sampling; cool to 4°C ± 2ºC	28 days

[1] Heated purge is considered a significant modification to the method, as per Section 11.3.1.1.
[2] Refer to Appendix 4 for details on sample collection or optional collection/storage devices.

9.0 PROCEDURE

9.1 **Sample Preparation and Purging**

9.1.1 It is highly recommended that all samples be screened prior to analysis. This screening step may be analysis of a soil/sediment sample's methanol extract (diluted), the headspace method (SW-846 method 3810), or the hexadecane extraction and screening method (SW-846 Method 3820). For soil/sediment samples, headspace screening of the unpreserved vial (obtained for the purposes of determining soil/sediment moisture content) is also an option.

9.1.2 Water Samples

Introduce volatile compounds into the gas chromatograph using a purge-and-trap concentrator.

9.1.2.1 For a manual load system, remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one 40-mL vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. This second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 20-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hours. Care must be taken to prevent air from leaking into the syringe.

Alternatively, commercially-available auto-samplers may be used to automatically introduce a 5.0 mL sample aliquot directly from a 40 mL sampling vial to the system for purging. Follow manufacturer's instructions for operation. In some cases, concentrations of surrogates and/or matrix spikes may need to be modified to accommodate the fixed injection volumes associated with automated sample-introduction systems.

9.1.2.2 If necessary, samples should be diluted prior to injection into the purge chamber. In such cases, all steps must be performed without delay until the diluted sample is in a gas-tight syringe.

9.1.2.2.1 Dilutions may be made in volumetric flasks (10 mL to 100 mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for highly concentrated samples.

9.1.2.2.2 Calculate the approximate volume of reagent water to be added to the volumetric flask selected and add slightly less than this volume of reagent water to the flask.

9.1.2.2.3 Inject the proper aliquot of sample from the syringe prepared in Section 9.1.2.1 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with reagent water. Cap the flask and invert three times. Repeat the above procedure for additional dilutions. Alternatively the dilutions can be made directly in the glass syringe to avoid further loss of volatiles.

9.1.2.2.4 Fill a 5-mL syringe with diluted sample as in Paragraph 9.1.2.1.

9.1.2.3 Add 4.0 µL of the surrogate spiking solution through the valve bore of the syringe. Close the valves.

9.1.2.4 If matrix spike analysis is to be performed, add 4.0 µL of the matrix spiking solution through the valve bore of the syringe. Close the valves.

9.1.2.5 Attach the syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

9.1.2.6 Close both valves and purge the sample for 11 min. Recommended purge-and-trap operating parameters are provided in Table 5.

9.1.2.7 At the conclusion of the purge time, attach the trap to the chromatograph (if necessary), adjust the device to the desorb mode, and begin the gas chromatographic temperature program and GC data acquisition. Concurrently, introduce the trapped materials to the gas chromatographic column by rapidly

heating the trap to 260°C and backflushing the trap with inert gas between 15 and 20 mL/min for 4 minutes.

9.1.2.8 While the trap is desorbing into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of reagent water (or methanol followed by reagent water) to avoid carryover of pollutant compounds into subsequent analyses.

Table 5. Recommended Purge and Trap Operating Parameters

Purge gas	Helium
Purge gas flow rate (mL/min)	40
Purge time (min)	11.0 ± 0.1
Purge temperature	Ambient*
Desorb temperature °C	260
Backflush inert gas flow (mL/min)	15-20
* If heated purge temperature is used, different preservation procedures apply; see Table 4. Heated purge is considered a significant modification to the method, as per Section 11.3.1.1.	

9.1.2.9 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the PURGE mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 260°C. After approximately 7 to 15 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. After a highly concentrated sample, a longer baking time may be necessary. When cool, the trap is ready for the next sample.

9.1.2.10 If the concentration of an analyte or hydrocarbon fraction in a sample exceeds the calibration range, a dilution of the sample is required. If a sample analysis results in a saturated detector response for a compound, the analysis must be followed by a blank reagent water analysis. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank demonstrates the lack of system interferences.

9.1.2.11 All dilutions should keep the detector response of the Target Analytes (previously saturated peaks) in the upper half of the linear range of the calibration curve.

9.1.2.12 Following sample analysis, measure and record the pH of the remaining sample.

9.1.3 Soil/Sediments

Soil and sediment samples are extracted with methanol. An aliquot of the extract is added to reagent water and introduced into the gas chromatograph using a purge-and-trap concentrator.

9.1.3.1 Weigh the sample vial to 0.1 g on a top loading balance and determine the weight of the soil/sediment sample; this determination requires knowledge of the empty/tared weight of the sample vial and volume/weight of methanol preservative that was added to the sample vial.

9.1.3.2 Add 1.0 mL of the surrogate spiking solution through the septum. The concentration and/or volume of the surrogate spiking solution may need to be increased for samples that are highly contaminated (based upon screening and/or field notes), to prevent dilution to below detectable limits.

9.1.3.3 If matrix spike analysis is to be performed, add 1.0 mL of the matrix spiking solution through the septum.

9.1.3.4 Agitate sample to facilitate adequate mixing of spiking solution(s) .

9.1.3.5 Allow soil/sediment to settle until a layer of methanol is apparent.

9.1.3.6 Using a microliter syringe, withdraw an appropriate aliquot of the methanol extract for sparging through the septum of the container. Sample screening data can be used to determine the volume of methanol extract to add to the 5 mL of reagent water for analysis. All dilutions must keep the response of the major constituents in the upper half of the linear range of the calibration curve.

9.1.3.7 Remove the plunger from one 5.0-mL Luerlock type syringe equipped with a syringe valve and fill until overflowing with reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to allow for addition of the extract (e.g., for 100 µL of extract adjust to 4.9 mL). Pull the plunger to 5.0 mL for addition of the sample extract. Add the volume of methanol extract determined from screening (recommended 100 µL if dilution not required).

9.1.3.8 Attach the syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber. Complete operations as specified in Paragraphs 9.1.2.6 through 9.1.2.11.

9.1.4 Proceed with the analysis as described in Sections 9.2 through 9.5. Analyze all laboratory method blanks and QC samples under the same conditions as that used for samples.

9.1.5 If the responses exceed the calibration or linear range of the system, use a smaller aliquot of methanol or aqueous sample.

9.1.6 Determination of Percent Moisture

9.1.6.1 Soil and sediment results must be reported on a dry-weight basis.

Transfer 5 to 10 g of sample into a tared (± 0.1 g) crucible. This sample must be obtained from a vial or container that does not contain methanol. Dry this 5 to 10 g sample overnight at 105°C, and reweigh (± 0.1 g). Allow to cool in a desiccator before reweighing. Calculate the percent moisture of the sample using the equation provided in Section 9.6.2.1 (Equation 9). Refer to ASTM Method D2216, Determination of Moisture Content of Soils and Sediments, for more detailed analytical and equipment specifications.

9.2 **Analytical Conditions**

9.2.1 Recommended analytical conditions are presented below. A chromatographic column with equivalent chromatographic properties, as described in Section 6.3.2, or alternative chromatographic conditions may be substituted to improve resolution of volatile petroleum hydrocarbons.

Chromatographic Column:	105 m x 0.53 mm I.D., 3.0 µm Restek Rtx- 502.2
Oven Temperature Program	Initial oven temperature 45°C, hold time 1 min; to 100 °C @ 3°C/min, hold time 0 min to 160°C @ 8 °C/min, hold time 0 min to 230 °C @ 20°C/min, hold time 7.5 min
Gas Flow Rates:	Carrier gas - Helium @ 12.5 mL/ min Oxidizer - Air @ 350 mL/min Fuel - Hydrogen @ 30 mL/min Make up - Air @ 17.5 mL/min
Injection Port Temperature:	250°C
Column Inlet Pressure:	20 p.s.i.g.

Detector Temperature: 230°C (PID)
230°C (FID)

9.3 **Retention Time Windows**

9.3.1 Before establishing retention time windows, optimize the GC system's operating conditions. Make three injections of the VPH Component Standard over the course of a 72-hr period. Serial injections over less than a 72-hr period may result in retention time windows that are too restrictive.

9.3.2 Calculate the standard deviation of the three absolute retention times for each individual compound in the VPH Component Standard.

9.3.3 The retention time window is defined as plus or minus three times the standard deviation of the absolute retention times for each compound in the VPH Component Standard. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

9.3.4 In those cases where the standard deviation for a particular standard is zero, the laboratory should substitute the standard deviation of a closely eluting structurally similar compound to develop a representative statistically-derived retention time window.

9.3.5 The laboratory must calculate retention time windows for each compound in the VPH Component Standard on each GC column and whenever a new GC column is installed. These data must be retained by the lab.

9.3.6 VPH retention time (Rt) windows of the aliphatic ranges are defined as beginning 0.1 minutes before the Rt of the beginning marker compound and ending 0.1 before the Rt of the ending marker compound, except for C_9, which is both a beginning and ending marker compound for two different ranges.

The C_5 - C_8 Aliphatic Hydrocarbon range ends immediately (0.1 min) before the elution of the n-C_9 peak. The C_9 - C_{12} Aliphatic Hydrocarbon range begins 0.1 min before the elution of n-C_9; therefore there is no overlap of the two ranges and the n-C_9 peak is only included in the C_9 - C_{12} Aliphatic Hydrocarbon range.

The VPH retention time (Rt) window for the C_9 - C_{10} Aromatic Hydrocarbons is defined as beginning 0.1 minutes after the Rt of the beginning marker compound and ending 0.1 before the Rt of the ending marker compound.

VPH marker compounds and windows are summarized in Table 6.

Table 6. VPH Marker Compounds

Hydrocarbon Range	Beginning Marker	Ending Marker
C_5-C_8 Aliphatic Hydrocarbons (FID)	0.1 min before n-Pentane	0.1 min before n-Nonane
C_9-C_{12} Aliphatic Hydrocarbons (FID)	0.1 min before n-Nonane	0.1 min before Naphthalene[1]
C_9-C_{10} Aromatic Hydrocarbons (PID)	0.1 min after o-xylene	0.1 min before Naphthalene

[1] The retention time for Dodecane (C_{12}) is approximately 2 minutes less than the retention time for naphthalene, using the column and chromatographic conditions recommended for this method. For simplicity, naphthalene is used as the ending marker for the C_9 - C_{12} Aliphatic Hydrocarbon range.

9.4 **Calibration**

9.4.1 Internal Standard Calibration Procedure

An internal standard calibration procedure is not recommended for this method.

9.4.2 External Standard Calibration Procedure

The use of Calibration Factors (CF) is the preferred approach to determine the relationship between the detector response and the analyte and collective range concentrations. It is also permissible to utilize linear regression to calculate the slope and y-intercept that best describes the linear relationship between the analyte and collective range concentrations and the instrument response. The linear regression approach for analytes and collective ranges is described in Appendix 6.

9.4.2.1 Prepare VPH Calibration Standards at a minimum of five concentration levels in accordance with the procedures and specifications contained in Section 7.0.

9.4.2.2 Analyze each VPH Calibration Standard following the procedures outlined in Section 9.5. Tabulate the area responses against the concentration injected. The ratio of area response to the concentration injected, defined as the calibration factor (CF), may be calculated for Target VPH analytes using Equation 1. The percent relative standard deviation (%RSD) of the calibration factor must be equal to or less than 25% over the working range for the analyte of interest, as determined using Equation 2. When this condition is met, linearity through the origin may be assumed, and the average calibration factor is used in lieu of a calibration curve.

Equation 1: Calibration Factor; VPH Target Analytes

$$Calibration\ Factor\ (CF) = \frac{area\ \ of\ \ peak}{concentration\ \ purged\ (\mu g / L)}$$

Equation 2: Percent Relative Standard Deviation

$$\%RSD = \frac{Stand\ \ Dev\ of\ \ 5\ CFs}{Mean\ of\ \ 5\ CFs}\ x\ 100$$

9.4.2.3 A collective calibration factor must also be established for each hydrocarbon range of interest. Calculate the collective CFs for C_5-C_8 Aliphatic Hydrocarbons and C_9-C_{12} Aliphatic Hydrocarbons using the FID chromatogram. Calculate the collective CF for the C_9-C_{10} Aromatic Hydrocarbons using the PID chromatogram. Tabulate the summation of the peak areas of all components in that fraction (i.e. C_5-C_8 Aliphatic Hydrocarbons, 3 components) against the total concentration injected. The results can be used to calculate the ratio of the peak area response summation to the concentration injected, defined as the CF, for the hydrocarbon ranges using Equation 3. The %RSD of the calibration factor must be equal to or less than 25% over the working range for the hydrocarbon range of interest, as determined using Equation 2.

Note: Do not include the area of any surrogate standard in calculating a Range CF. Do not include the area of naphthalene when determining the CF for C_9 - C_{10} Aromatic Hydrocarbons.

Equation 3: Range Calibration Factor: Hydrocarbon Ranges

$$Range\ CF = \frac{Area\ summation\ of\ \ range\ components}{Total\ concentration\ \ purged\ (\ \mu g\ /\ L)}$$

9.4.2.4 At a minimum, the working calibration factor must be verified on each working day, after every 20 samples, and at the end of the analytical sequence by the injection of a mid-level continuing calibration standard to verify instrument performance and linearity. If the percent difference (%D) for any analyte varies from the predicted response by more than ±25%, as determined using Equation 4, a new five-point calibration must be performed for that analyte. Greater percent differences are permissible for n-nonane. If the %D for n-nonane is greater than 30, note the nonconformance in the case narrative. It should be noted that the %Ds are calculated when CFs are used for the initial calibration and percent drifts (Equation 6-5, Appendix 6) are calculated when calibration curves using linear regression are used for the initial calibration.

Equation 4: Percent Difference (%D)

$$\%D = \frac{CF_{AVG} - CF_{CC}}{CF_{AVG}}\ x\ 100$$

where:

CF_{AVG} = Average Calibration Factor calculated from initial calibration.

CF_{CC} = Calibration Factor calculated from continuing calibration standard.

9.4.2.5 Target VPH Analytes and C_9 to C_{10} Aromatic Hydrocarbons are quantitated on the PID chromatogram.

9.4.2.6 C_5 through C_8 and C_9 through C_{12} Aliphatic Hydrocarbons are quantitated on the FID chromatogram.

9.5 **GC Analysis**

9.5.1 Samples are analyzed in a group referred to as an analytical batch. The analytical sequence begins with instrument calibration (initial or continuing) followed by up to 20 samples interspersed with blanks and QC samples and closed with a mid-range continuing calibration standard. The analytical sequence ends when one or more analytical batches have been processed or when any required qualitative and/or quantitative QC criteria are exceeded.

9.5.2 Samples are introduced into the gas chromatograph using a purge-and-trap concentrator.

9.5.3 Water samples are directly injected into the purging chamber using a 5-mL syringe. Soil/sediment samples are extracted in methanol, the methanol extract is mixed with reagent water, and the methanol/water mixture is injected into the purging chamber using a 5-mL syringe.

9.5.4 Establish daily retention time windows for each analyte of interest. Use the absolute retention time for each analyte in the continuing calibration standard as the midpoint of the window for that day. The daily retention time window equals the midpoint ± three times the standard deviation determined in Section 9.3.

9.5.4.1 Tentative identification of a VPH target analyte occurs when a peak from a sample chromatogram falls within the daily retention time window. Confirmation on a second GC column or by GC/MS analysis may be necessary, if warranted by the project's data quality objectives.

9.5.4.2 Co-elution of the p- and m- xylene isomers may occur.

9.5.4.3 Validation of GC system qualitative performance must be accomplished by the analysis of mid-level standards within the analysis sequence. If the retention times of the Target VPH Analytes fall outside their daily retention time window in the standards, the system is out of control. In such cases, the cause of the non-conformance must be identified and corrected.

9.5.5 Aliphatic and aromatic ranges of interest are determined by the collective integration of all peaks that elute between specified range "marker" compounds. Due to the variability in software approaches and applications to collective peak area integration, it is recommended that a manual verification be initially performed to document accurate integration.

9.5.6 **When quantifying on a peak area basis by external calibration, collective peak area integration for the hydrocarbon ranges must be <u>from baseline</u> (i.e. must include the unresolved complex mixture "hump" areas).** For the integration of individual Target VPH Analytes, surrogate compounds, and internal standards, a valley-to-valley approach should typically be used, though this approach may be modified on a case-by-case basis by an experienced analyst. In any case, the unresolved complex mixture "hump" areas must <u>not</u> be included in the integration of individual Target VPH Analytes and surrogate compounds.

9.5.7 If the Target VPH Analytes are to be quantified using this method, and the response for an individual analyte exceeds the linear range of the system, dilute the sample and reanalyze. The samples must be diluted so that all peaks fall within the linear range of the detector.

9.5.8 For non-target analytes eluting in the aliphatic or aromatic fractions, the upper linear range of the system should be defined by peak height measurement, based upon the maximum peak height documented for an aliphatic or aromatic standard within the fraction that is shown to be within the linear range of the detector.

9.5.9 Under circumstances that sample dilution is required because either the concentration of one or more of the target analytes exceed the concentration of their respective highest calibration standard or any non-target peak eluting within any aliphatic or aromatic range exceeds the peak height documented for the highest range-specific calibration standard, the Reporting Limit (RL) for each target analyte and/or range must be adjusted (increased) in direct proportion to the Dilution Factor (DF). Where:

$$DF = \frac{\text{Sample Aliquot Volume (mL) + Diluent Volume (mL)}}{\text{Sample Aliquot Volume (mL)}}$$

And the revised RL for the diluted sample, RL_d:

RL_d = DF X Lowest Calibration Standard for Target Analyte

It should be understood that samples with elevated RLs as a result of a dilution may not be able to satisfy "MCP program" reporting limits in some cases if the RL_d is greater than the applicable MCP standard or criterion to which the concentration is being compared. Such increases in RLs are the unavoidable but acceptable consequence of sample dilution that enable quantification of target analytes which exceed the calibration range. All dilutions must be fully documented in the Laboratory Case Narrative.

<u>Analytical Note</u>: Over dilution is an unacceptable laboratory practice. The post-dilution concentration of the highest concentration target analyte must be at least 60 - 80% of its

highest calibration standard. This will avoid unnecessarily high reporting limits for other target analytes which did not require dilution.

9.6 Calculations

The concentration of Target VPH Analytes and hydrocarbon ranges in a sample may be determined by calculating the concentration of the analyte or hydrocarbon range purged, from the peak area response, using the calibration factor determined in Section 9.4. If linear regression was used for calibration, refer to Appendix 6 for sample concentration calculations.

9.6.1 Aqueous samples

The concentration of a specific analyte or hydrocarbon range in an aqueous sample may be calculated using Equations 5 and 6, respectively.

Equation 5: Aqueous Samples; Target VPH Analytes

$$Conc\ Analyte\ (\mu g/L) = \frac{(A_x)(D)}{(CF)}$$

Equation 6: Aqueous Samples: Hydrocarbon Ranges

$$Conc\ HC\ Range\ (\mu g/L) = \frac{(A_x)(D)}{(Range\ CF)}$$

where:

A_x = Response for the analyte or hydrocarbon range in the sample. Units are in area counts for Target VPH Analytes and the hydrocarbon ranges.

D = Dilution factor; if no dilution was made, D = 1, dimensionless.

CF = Average Calibration Factor for Target VPH Analyte, determined in Section 9.4.2.2.

Range CF = Average Calibration Factor for hydrocarbon range, determined in Section 9.4.2.3.

9.6.2 Non-Aqueous Samples (Methanol Extraction)

The concentration of a specific analyte or hydrocarbon range in a soil or sediment sample may be calculated using Equations 7 and 8, respectively.

Equation 7: Non-Aqueous Samples; Target VPH Analytes

$$Conc\ Analyte\ (\mu g/kg) = \frac{(A_x)(V_t)(D)(V_w)}{(V_i)(W_d)(CF)}$$

Equation 8: Non-Aqueous Samples: Hydrocarbon Ranges

$$Conc\ HC\ Range\ (\mu g/kg) = \frac{(A_x)(V_t)(D)(V_w)}{(V_i)(W_d)(Range\ CF)}$$

where: A_x, CF, Range CF, and D have the same definition as for aqueous samples, and

V_t = Total volume of methanol extract, mL

Analytical Note: This volume must also include the 1.0 mL surrogate spiking solution added to soil/sediment samples and the volume of water added due to % moisture correction. See Section 9.6.2.2.

V_i = Volume of methanol extract added to reagent water for purge-and-trap analysis, µL.

V_w = Volume of reagent water used for purge-and-trap analysis, µL.

W_d = Dry weight of sample, g (see Equations 9 through 11)

9.6.2.1 Calculation of Dry Weight of Sample

In order to calculate the dry weight of sample purged (W_d), it is necessary to determine the moisture content of the soil/sediment sample, using the procedure outlined in Section 9.1.6. Using the data obtained from Section 9.1.6, W_d is calculated using Equations 9 through 11.

Equation 9: Percent Moisture

$$\%\ Moisture = \frac{g\ wet\ sample - g\ dry\ sample}{g\ wet\ sample}\ X\ 100$$

Equation 10: Percent Solids

$$\%\ Dry\ Solids\ =\ (100)\ -\ (\%\ Moisture)$$

Equation 11: Dry Weight of Sample

$$W_d\ (g)\ =\ (\%\ Dry\ Solids\ /\ 100)(g\ of\ extracted\ sample)$$

9.6.2.2 Data Correction for VPH Target Analyte and Range Calculations for Methanol Preservation Dilution Effect

Based on the requirements of SW-846 Method 8000C, Section 11.10.05, VPH analytical results for soil/sediment samples must be corrected for the Methanol Preservation Dilution Effect. The potential for under reporting VPH Target Analyte and Hydrocarbon Range concentrations is more pronounced as the "as-received" % moisture content of the soil/sediment sample increases, if this correction is neglected.

VPH Target Analyte and Hydrocarbon Range concentrations in solid samples preserved with methanol are subject to a systematic negative bias if the potential increase of the total solvent volume during the methanol extraction process is not considered. This increase in extraction solvent volume is a direct result of the solubility of the entrained sample moisture (water) in the methanol. The total solvent volume is the additive sum of the volume of methanol and the entrained sample moisture that partitions into the methanol during extraction. The volume of water partitioned is estimated from the % moisture determination (and the assumption that 1 g of water occupies a volume of 1 mL). This is a

conservative correction regarding calculated VPH concentrations because some fraction of the sample's % moisture may not partition into the methanol, due to various physiochemical binding forces. The total solvent/water volume (Vt) is calculated as follows:

Equation 12: Calculation of Solvent/Water Volume

mL solvent/water (Vt) = mL of methanol + ((% moisture/100) × g of sample)

This "corrected" Vt value should be substituted directly for the Vt value shown in Section 9.6.2, Equations 7 and 8, above. It should be noted that whether corrected or uncorrected, the Vt value used in Equations 7 or 8 to calculate VPH concentrations must also include the 1.0 mL surrogate spiking solution added to soil/sediment samples.

10.0 QUALITY CONTROL

10.1 General Requirements and Recommendations

10.1.1 Each laboratory that uses this method is required to operate a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability (IDLC) and an ongoing analysis of spiked samples to evaluate and document the quality of data. The initial demonstration of laboratory capability should be repeated whenever new staff are trained or significant changes in instrumentation or the method (i.e., new extraction method, etc.) are made. The laboratory must maintain records to document data quality. Ongoing data quality checks are compared with established performance criteria to determine if the results of analyses meet the performance standards for the method. When results of sample spikes indicate atypical method performance, a quality control check standard must be analyzed to confirm that the analytical system was in-control when the measurements were performed.

10.1.2 A methanol trip blank or acidified reagent water trip blank **should** continually accompany each soil/sediment sample or water sample batch, respectively, during sampling, storage, and analysis. Refer to CAM-VII A for **required** frequency of trip blanks.

10.1.3 A Laboratory Method Blank must be run after samples suspected of being highly contaminated to determine if sample carryover has occurred.

10.1.4 At a minimum, for each analytical batch (up to 20 samples of similar matrix), a beginning Initial Calibration or Opening mid-range Continuing Calibration Standard, Closing mid-range Continuing Calibration Standard, Laboratory Method Blank, Laboratory Control Sample (LCS) and LCS Duplicate must be analyzed. Matrix Duplicates, Matrix Spike (MS) and/or MS duplicates should be analyzed, at the request of the data user, based upon the nature of the sample. For analytical batches with more than 10 samples, the analysis of an additional mid-range Continuing Calibration Standard should also be considered. However, it should be noted that the analysis of the Continuing Calibration Standard is required prior to sample analysis, after every 20 samples, and at the end of an analytical sequence, at a minimum. The blank and quality control samples fortified with known concentrations and volumes of analytical standards should be carried through the complete sample preparation and measurement processes.

10.1.5 The recommended sequence of analysis is as follows:

(1) Analytical Batch Opening Initial Calibration or mid-range Continuing Calibration Standard **[REQUIRED]**
(2) Analytical Batch Laboratory Control Sample **[REQUIRED]**
(3) Analytical Batch Laboratory Method Blank **[REQUIRED]**
(4) Up to 20 Samples
(5) Matrix Duplicate sample [As requested by data user]

(6) Matrix Spike/MS Duplicate [As requested by data user]
(7) Optional mid-range Continuing Calibration Standard (consider after 10 samples)
(8) Analytical Batch Laboratory Control Sample Duplicate [a] **[REQUIRED**
(9) Closing mid-range Continuing Calibration Standard [b] after 20 samples and at end of analytical batch **[REQUIRED]**

a. May be used as the Analytical Batch Laboratory Control Sample for the next analytical batch if batches are processed continuously.
b. May be used as Analytical Batch Opening Continuing Calibration for the next analytical batch if batches are processed continuously.

10.1.6 It is recommended that surrogate standard recoveries be monitored and documented on a continuing basis. At a minimum, when surrogate recovery from a sample, blank, or QC sample is less than 70% or more than 130%, check calculations to locate possible errors, check the fortifying standard solution for degradation, and check changes in instrument performance. If the cause cannot be determined, reanalyze the sample unless one of the following exceptions applies:

(1) Obvious interference is present on the chromatogram (e.g., unresolved complex mixture);
(2) Percent moisture of associated soil/sediment sample is >25% and surrogate recovery is >10%; or
(3) The surrogate exhibits high recovery and associated target analytes or hydrocarbon ranges are not detected in sample.

If a sample with a surrogate recovery outside of the acceptable range is not reanalyzed based on any of these aforementioned exceptions, this information must be noted on the data report form and discussed in the Environmental Laboratory Case Narrative.

Analysis of the sample on dilution may diminish matrix-related surrogate recovery problems. This approach can be used as long as the reporting limits to evaluate applicable MCP standards can still be achieved with the dilution. If not, reanalysis without dilution must be performed.

10.2 **Minimum Instrument QC**

10.2.1 The n-pentane (C_5) and MtBE peaks must be adequately resolved from any solvent front that may be present on the FID and PID chromatograms, respectively. This is achievable using the recommended chromatographic column and purge-and-trap procedures. Coelution of the m- and p- xylene isomers is permissible. All surrogates must be adequately resolved from individual Target Analytes included in the VPH Component Standard.

For the purposes of this method, adequate resolution is assumed to be achieved if the height of the valley between two peaks is less than 25% of the average height of the two peaks.

10.2.2 Retention time windows must be re-established for each Target VPH Analyte each time a new GC column is installed, and must be verified and/or adjusted on a daily basis. (See Sections 9.3 and 9.5.4)

10.2.3 Calibration factors must be developed based upon the analysis of calibration standards prepared at a minimum of 5 concentration levels. The linearity of calibration factors may be assumed if the %RSD over the working range of the curve is less than or equal to 25%.

10.3 **Initial and Periodic Method Demonstration of Laboratory Capability (IDLC)**

The QC procedures described in Appendix 7 and described in SW-846 Method 8000B, Section 8.4 must be conducted, successfully completed and documented as an initial demonstration of laboratory capability, prior to the analysis of any samples by the VPH Method. Subsequent to this initial demonstration, additional evaluations of this nature should be conducted on a periodic basis, in response to changes in instrumentation or operations, training new analysts and/or in response to confirmed or suspected systems, method, or operational problems. Elements of the Initial Demonstration of Laboratory Capability include:

10.3.1 Demonstration of Acceptable System Background, see Appendix 7, Section 2.0 (Optional)

10.3.2 Initial Demonstration of Accuracy (IDA), see Appendix 7, Section 3.0

10.3.3 Initial Demonstration of Precision (IDP), see Appendix 7, Section 4.0, and

10.3.4 Method Detection Limit (MDL), see Appendix 7, Section 5.0 (Optional)

10.4 **Ongoing Method QC Demonstrations**

10.4.1 Each sample, blank, LCS, LCSD, MS, and Matrix Duplicate must be fortified with the surrogate spiking solution. Required surrogate recovery is 70% to 130%. At a minimum, when surrogate recovery from a sample, blank, or QC sample is less than 70% or more than 130%, check calculations to locate possible errors, check the fortifying solution for degradation, and check for changes in instrument performance. If the cause cannot be determined, reanalyze the sample unless one of the following exceptions applies:

(1) Obvious interference is present on the chromatogram (e.g., unresolved complex mixture);
(2) Percent moisture of associated soil/sediment sample is >25% and surrogate recovery is >10%; or
(3) The surrogate exhibits high recovery and associated target analytes or hydrocarbon ranges are not detected in sample.

If a sample with a surrogate recovery outside of the acceptable range is not reanalyzed based on any of these aforementioned exceptions, this information must be noted on the data report form and discussed in the Environmental Laboratory Case Narrative.

Analysis of the sample on dilution may diminish matrix-related surrogate recovery problems. This approach can be used as long as the reporting limit for the applicable MCP standards will still be achieved with the dilution. If not, reanalysis without dilution must be performed. Recoveries outside of the acceptable range after reanalysis must also be noted on the data report form and discussed in the Environmental Laboratory Case Narrative.

10.4.2 At a minimum, with every batch of 20 samples or less the laboratory must analyze the following:

10.4.2.1 **Continuing Calibration Standard** - A mid-range continuing calibration standard, prepared from the same stock standard solution used to develop the calibration curve, must be analyzed prior to sample analysis to verify the calibration state of the instrument. For large analytical batches that contain more than 10 samples, the analysis of an additional mid-range continuing calibration standard is recommended after the analysis of the tenth sample. However, it should be noted that a mid-range continuing calibration standard is required after every 20 samples and at the end of the analytical sequence. If the percent difference or percent drift of any analyte within the continuing calibration standard varies from the predicted response by more than 25%, a new five-point calibration must be performed for

that analyte. Greater differences are permissible for n-nonane (if included in the calibration of the C_9-C_{12} aliphatic range). If the percent difference or percent drift is greater than 30 for n-nonane, note the nonconformance in the narrative.

10.4.2.2 **Laboratory Method Blank** - A water or soil Laboratory Method Blank is prepared by fortifying a 5 mL reagent water blank with 4 µL of the surrogate spiking solution (for water samples), or by fortifying 25 ml of methanol with 1.0 mL of the surrogate spiking solution (for soil/sediment samples). Peaks must not be detected above the Reporting Limit within the retention time window of any analyte of interest. The hydrocarbon ranges must not be detected at a concentration greater than 10% of the most stringent MCP cleanup standard.

10.4.2.3 **Laboratory Control Sample** - A Laboratory Control Sample is prepared by fortifying a 5 mL reagent water blank with 4 µL of the matrix spiking solution (for water samples), or by fortifying 25 mL of methanol with 1.0 mL of the matrix spiking solution (for soil/sediment samples). The spike recovery must be between 70% and 130%. Lower recoveries of n-nonane are permissible (if included in the calibration of the C_9-C_{12} aliphatic range). If the recovery of n-nonane is <30%, note the nonconformance in the narrative.

10.4.2.4 **LCS Duplicate** – A Laboratory Control Sample Duplicate is prepared by fortifying a 5 mL reagent water blank with 4 µL of the matrix spiking solution (for water samples), or by fortifying 25 mL of methanol with 1.0 mL of the matrix spiking solution (for soil/sediment samples). The LCS Duplicate is prepared separately from the LCS but prepared and analyzed in the same manner as the LCS and is used as the data quality indicator of precision. The Analytical Batch Precision is determined from the Relative Percent Difference (RPD) of the concentrations (not recoveries) of LCS/LCSD pair. The RPD for individual Target VPH Analytes and aliphatic and aromatic hydrocarbon range concentrations must be less than or equal to 25.

10.4.3 At the request of the data user, and in consideration of sample matrices and data quality objectives, matrix spikes and matrix duplicates may be analyzed with every batch of 20 samples or less per matrix.

10.4.3.1 **Matrix duplicate** - Matrix duplicates are prepared by analyzing one sample in duplicate. The purpose of the matrix duplicates is to determine the homogeneity of the sample matrix as well as analytical precision. The RPD of detected results in the matrix duplicate samples must not exceed 50 when the results are greater than 5x the reporting limit.

10.4.3.2 **Matrix Spike/Matrix Spike Duplicate** - The water or soil matrix spike is prepared by fortifying an actual 5 mL water sample with 4 µL of the matrix spiking solution, or by fortifying an actual 15-25 g soil sample with 1.0 mL of the matrix spiking solution (see Section 7.6). The desired spiking level is 50% of the highest calibration standard. However, the total concentration in the MS (including the MS and native concentration in the unspiked sample) should not exceed 75% of the highest calibration standard in order for a proper evaluation to be performed. The purpose of the matrix spike is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate unspiked aliquot and the measured values in the matrix spike corrected for background concentrations. The corrected concentrations of each analyte within the matrix spiking solution must be within 70 - 130% of the true value. Lower recoveries of n-nonane are permissible (if included in the calibration of the C_9-C_{12} aliphatic range), but must be noted in the narrative if <30%.

10.4.4 If any of the performance standards specified in Section 10.4.1 and 10.4.2 are not met, the cause of the non-conformance must be identified and corrected before any additional samples may be analyzed. Any samples run between the last QC samples that met the

criteria and those that are fallen out must be rerun. These QC samples include the opening continuing calibration standard, laboratory method blank, LCS, LCSD, and closing continuing calibration standard. If this is not possible, that data must be reported as suspect.

11.0 DATA PRODUCTION AND REPORTING

11.1 **Calibration**

Using the external calibration procedure (See Section 9.4.2) calibrate the GC as follows:

11.1.1 Using the PID chromatogram, calculate an average CF or linear regression (LR) calibration curve for the Target VPH Analytes (benzene, toluene, ethylbenzene, m,p,o-xylenes, naphthalene, and methyl-t-butylether). This step is not necessary if these Target Analytes will not be individually identified and quantitated by the VPH method (i.e., if unadjusted values only will be reported for the hydrocarbon ranges or if reporting concentrations of Target VPH Analytes via another method).

11.1.2 Using both the FID and PID chromatograms, calculate an average CF for the surrogate 2,5-dibromotoluene.

11.1.3 Using the FID chromatogram, calculate an average collective CF for the total concentration of the C_5 - C_8 Aliphatic Hydrocarbons. Tabulate the collective peak area response of the 3 components (n-pentane, 2-methylpentane, 2,2,4-trimethylpentane) against the collective concentration injected.

11.1.4 Using the FID chromatogram, calculate an average collective CF for the total concentration of C_9 - C_{12} Aliphatic Hydrocarbons. Tabulate the collective peak area response of the 2 components (n-decane and n-butylcyclohexane) against the collective concentration injected. Alternatively, the CF for C_9 - C_{12} Aliphatic Hydrocarbons can be calculated using the collective area response of 3 components (n-nonane, n-decane and n-butylcyclohexane).

11.1.5 Using the PID chromatogram, calculate an average collective CF for the total concentration of C_9 - C_{10} Aromatic Hydrocarbons. This value is the value for 1,2,4-trimethylbenzene, the only aromatic standard within this range.

11.2 **Sample Analysis**

11.2.1 <u>PID Chromatogram</u>

11.2.1.1 If desired, determine the peak area count for the Target VPH Analytes.

11.2.1.2 Determine the peak area count for the surrogate 2,5-dibromotoluene.

11.2.1.3 Determine the total area count for all peaks eluting 0.1 minutes after the retention time (Rt) for o-Xylene and 0.1 minutes before the Rt for naphthalene.

11.2.1.4 Using the equations contained in Section 9.6, calculate the concentrations of the surrogate standard 2,5-dibromotoluene and C_9 through C_{10} Aromatic Hydrocarbons. Optionally, calculate the concentrations of the individual Target VPH Analytes.

11.2.2 <u>FID Chromatogram</u>

11.2.2.1 Determine the total area count for all peaks eluting 0.1 minutes before the Rt for n-pentane and 0.01 minutes before the Rt for n-nonane. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

11.2.2.2 Determine the total area count for all peaks eluting 0.01 minutes before the Rt for n-nonane and 0.1 before the Rt for naphthalene. It is not necessary to identify or quantitate individual aliphatic compounds within this range.

11.2.2.3 Determine the peak area count for the surrogate standard 2,5-dibromotoluene.

11.2.2.4 Using the equations contained in Section 9.6, calculate the concentrations of C_5 through C_8 Aliphatic Hydrocarbons, C_9 through C_{12} Aliphatic Hydrocarbons, and the surrogate standard 2,5-dibromotoluene.

11.2.3 Data Adjustments

11.2.3.1 By definition, the collective concentrations of aliphatic and aromatic fractions of interest **exclude** the individual concentrations of Target VPH Analytes. Accordingly, a series of data adjustment steps are necessary to adjust the collective range concentrations calculated in Section 11.2.2.4, to eliminate "double counting" of analytes.

11.2.3.2 The necessary data adjustment steps may be taken by the laboratory reporting the range concentration data, or by the data user. The extent of data adjustments taken by the laboratory must be noted on the data report form.

11.2.3.2.1 Subtract the area counts of the surrogate compound(s) from the collective area count of any range in which they elute. If the recommended surrogate 2,5-dibromotoluene is used, no correction is necessary, as this compound elutes after all ranges of interest.

11.2.3.2.2 Subtract the collective concentration of C_9-C_{10} Aromatic Hydrocarbons from the collective concentration of C_9-C_{12} Aliphatic Hydrocarbons. If this value is less than the Reporting Limit (RL), report "< RL" or "RL U", with a specific value replacing "RL" (e.g., "< 10" or "10 U").

11.2.3.2.3 Subtract the individual concentrations of the Target VPH Analytes from the appropriate aliphatic range (i.e., C_5 - C_8 or C_9 - C_{12} Aliphatic Hydrocarbons) in which they elute. Do not subtract any VPH Target Analyte concentration if this concentration is less than the RL (lowest calibration standard). If the individual concentrations of Target VPH Analytes have been quantitated using another method (e.g., by using an MS detector), note this on the data report form. If the individual concentrations of Target VPH Analytes have not been quantitated, report the values as Unadjusted C_5 - C_8 Aliphatic Hydrocarbons and Unadjusted C_9 - C_{12} Aliphatic Hydrocarbons, and indicate "Not Determined" for C_5 - C_8 Aliphatic Hydrocarbons and C_9 - C_{12} Aliphatic Hydrocarbons.

11.2.3.3 For purposes of compliance with the reporting and cleanup standards specified in the Massachusetts Contingency Plan, the concentration of Unadjusted C_5 - C_8 Aliphatic Hydrocarbons and Unadjusted C_9 - C_{12} Aliphatic Hydrocarbons may be conservatively deemed to be equivalent to the concentration C_5 - C_8 Aliphatic Hydrocarbons and C_9 - C_{12} Aliphatic Hydrocarbons.

11.3 Data Reporting Content

The required content for VPH Method data is presented in Appendix 3. This information provides data users with a succinct and complete summary of pertinent information and data, as well as a clear affirmation that the QC procedures and standards specified in this method were evaluated and achieved. Any significant modification to the MADEP VPH Method, as described in Section 11.3.1.1, and indicated by a negative response to Question D on the MADEP MCP ANALYTICAL METHOD REPORT CERTIFICATION FORM (also included in Appendix 3) precludes the affected data from achieving "Presumptive Certainty" status. If a significant modification to the VPH Method is utilized, an attachment to the analytical report must be included to demonstrate compliance with the method performance requirements of Section 1.12 on a matrix- and petroleum product-specific basis.

While it is permissible to modify the reporting format, all of the data and information specified in Appendix 3 for these reports must be provided in a clear, concise, and succinct manner.

11.3.1.1 "Significant Modifications" to this method shall include, without limitation, all of the following:

11.3.1.1.1 The use of alternative detectors to quantitate range concentrations;
11.3.1.1.2 The use of other than a purge-and-trap sample preparation procedure;
11.3.1.1.3 The use of a heated purge; or
11.3.1.1.4 Failure to provide all of the data and information presented in Appendix 3 as well as the required method deliverables discussed in Section 11.3.2.

NOTE: If alternate detectors are used, the laboratory must demonstrate that the performance standards listed in Section 1.12 were achieved.

11.3.1.2 Positive affirmation that all required QA/QC procedures and performance standards were followed and achieved means that all of the required steps and procedures detailed in Section 10.0 have been followed, and that all data obtained from these steps and procedures were within the acceptance limits specified for these steps and procedures.

11.3.2 In addition to sample results, the VPH data report must contain the following items

- Laboratory Method Blank Results
- Laboratory Control Sample Results
- Laboratory Control Sample Duplicate Results
- Matrix Spike and/or Matrix Spike Duplicate Results (only if requested by data user)
- Matrix Duplicate Results (only if requested by data user)
- Surrogate Spike Recoveries (for all field samples and QC samples)
- Results of reanalyses or dilutions must be reported as required in WSC-CAM-IV A, "Quality Assurance and Quality Control Requirements for the Method for the Determination of Volatile Petroleum Hydrocarbons (VPH), MADEP-VPH-03-1 for the Massachusetts Contingency Plan (MCP)", Table IV A-2.
- If a significant modification is utilized, demonstration of compliance with analytical performance standards specified in Section 1.12 on a matrix- and petroleum product-specific basis must be included as an attachment to the analytical report.

11.3.3 General laboratory reporting requirements are outlined in WSC-CAM-VII A, "Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data", Section 2.4. A copy of the required MADEP MCP Analytical Method Report Certification Form is included in Appendix 3 of this method.

12.0 REPORTING LIMITS

The Reporting Limits (RLs) for Target VPH Analytes shall be based upon the concentration of the lowest calibration standard for the analyte of interest. The RL must be greater than or equal to the concentration of the lowest calibration standard.

The RLs for hydrocarbon ranges shall be based upon the concentration of the lowest calibration standard for an individual analyte within the range of interest. The RL will be set at 100x the concentration of the lowest calibration standard for the associated analyte.

Based on a concentration of 1 µg/L for the lowest calibration standard for all analytes, the following reporting limits would be generated for the hydrocarbon ranges:

Aqueous Samples: Hydrocarbon range reporting limits would be equivalent to 100 µg/L.
Soil/Sediment Samples: Hydrocarbon range reporting limits would be equivalent to 5 mg/kg based on a 1:1 ratio of methanol: soil and analysis of a 100 µL aliquot of the methanol extract in 5 mL water.

13.0 METHOD PERFORMANCE

Single laboratory accuracy, precision and MDL data for method analytes are provided in Tables 1-1 through 1-2 in Appendix 1. Chromatograms are provided in Appendix 2.

14.0 REFERENCES

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14. Massachusetts DEP “Report on the Results of the Fall 1997 VPH/EPH Round Robin Testing Program”, December 1997.

15. EPA UST Workgroup, Draft “Method for Determination of Gasoline Range Organics”, November, 1990.

16 MADEP and ABB Environmental Services, Inc., "Interim Final Petroleum Report: Development of Health-Based Alternative to the Total Petroleum Hydrocarbon (TPH) Parameter", August, 1994.

17. MADEP, “Final Updated Petroleum Hydrocarbon Fraction Toxicity Values For the VPH/EPH/APH Methodology”, January 2003.

18. ASTM Method D2216-92, “Determination of Moisture Content of Soils and Sediments.”

APPENDIX 1

SINGLE LABORATORY ACCURACY, PRECISION, AND METHOD DETECTION LIMITS (MDL) DATA

Table 1-1. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Compounds in Component Standard Spiked Into Reagent Water and Analyzed by the VPH Method

Compound	Spiked Conc. (µg/L)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)		MDL[a] (µg/L)	
		PID[d]	FID[e]	PID	FID	PID	FID
n-Pentane	6.0		91		6.3		1.1
2-Methylpentane	8.0		100		8.6		2.2
Methyl-tert-butylether	3.0	95		5.2		0.47	
2,2,4-Trimethylpentane	4.0		98		11.9		1.5
Benzene	1.0	91		7.5		0.21	
Toluene	3.0	93		6.2		0.55	
n-Nonane	2.0		98		7.2		0.44
Ethylbenzene	1.0	92		5.6		0.16	
m- & p-Xylene	4.0	95		5.2		0.62	
o-Xylene	2.0	86		14.8		0.81	
1,2,4-Trimethylbenzene	2.0	89		6.1		0.34	
Naphthalene	4.0	113		11.1		1.57	
2,5-Dibromotoluene (surrogate)	40	90	90	10.9	13.3		

[a] Based on analysis of seven samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.

Table 1-2. Single Laboratory Accuracy, Precision, and Method Detection Limits (MDLs) for Compounds in Component Standard Spiked Into VPH-Free Sand and Analyzed by the VPH Method

Compound	Spiked Conc. (µg/g)	Method Accuracy[a] (Mean % Recovery[b])		Method Precision[a] (RSD[c] - %)		MDL[a] (µg/g)	
		PID[d]	FID[e]	PID	FID	PID	FID
n-Pentane	2		96		4.7		0.28
2-Methylpentane	3		99		5.1		0.47
Methyl-tert-butylether	3	89		4.7		0.39	
2,2,4-Trimethylpentane	3		110		2.1		0.22
Benzene	1	100		4.5		0.14	
Toluene	3	104		4.3		0.42	
n-Nonane	2		108		3.6		0.25
Ethylbenzene	1	103		5.0		0.16	
m- & p-Xylene	4	101		4.0		0.51	
o-Xylene	2	106		4.3		0.28	
1,2,4-Trimethylbenzene	2	103		3.8		0.25	
Naphthalene	2	86		2.8		0.15	
2,5-Dibromotoluene (surrogate)	2	95		11.4		0.68	

[a] Based on analysis of seven samples spiked with component standard.
[b] Recovery (%) of spiked concentration.
[c] RSD = relative standard deviation (%) of mean concentration measured.
[d] PID = photoionization detector.
[e] FID = flame ionization detector.

APPENDIX 2

CHROMATOGRAMS

Figure	Description
1	Gas Chromatogram (FID) for VPH Component Standard (20 ug/L Standard)
2	Gas Chromatogram (PID) for VPH Component Standard (20 ug/L Standard)
3	Gas Chromatogram (FID) of the VPH Gasoline Standard
4	Gas Chromatogram (PID) of the VPH Gasoline Standard

Gas Chromatograms of the VPH Component Standard (20 µg/L)

Restek RTX-502.2 capillary column (105 m x 0.53 mm i.d., 3-µm film thickness); PID (10.2 eV) in series with and FID (OI analytical); Tekmar (model 4000) purge-and-trap concentrator fitted with a custom absorbent trap packed with Carbopack B (Supelco); purge-and-trap and GC operating conditions as specified in Section 9.0 of the method. N-dodecane elutes at 31.2 minutes(not shown in chromatogram)

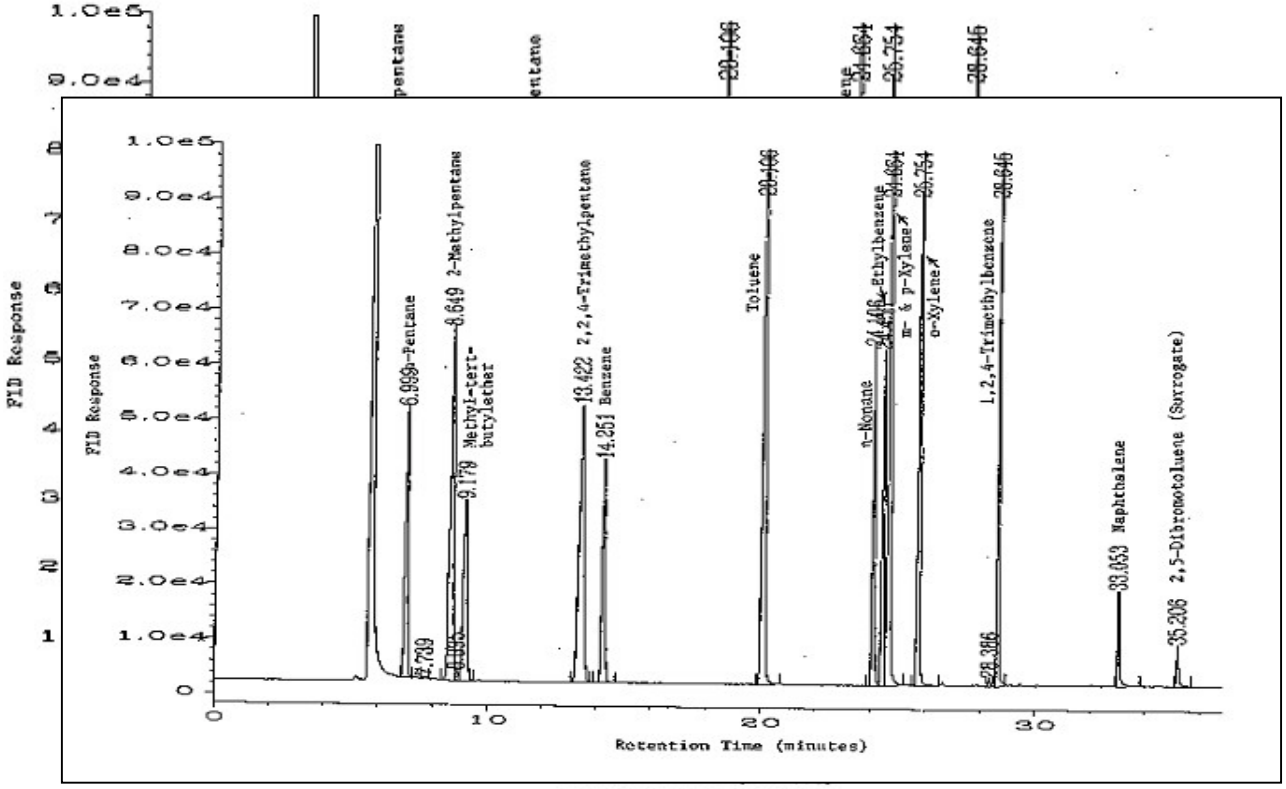
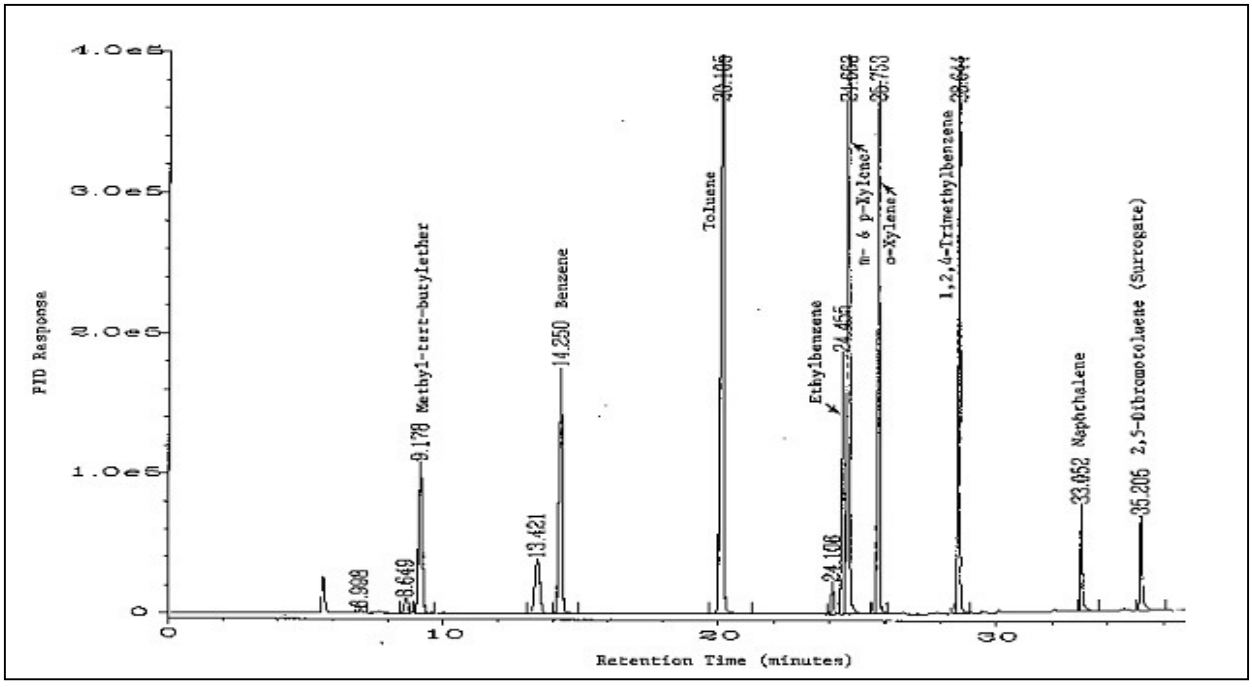


Figure 2. PID Chromatogram



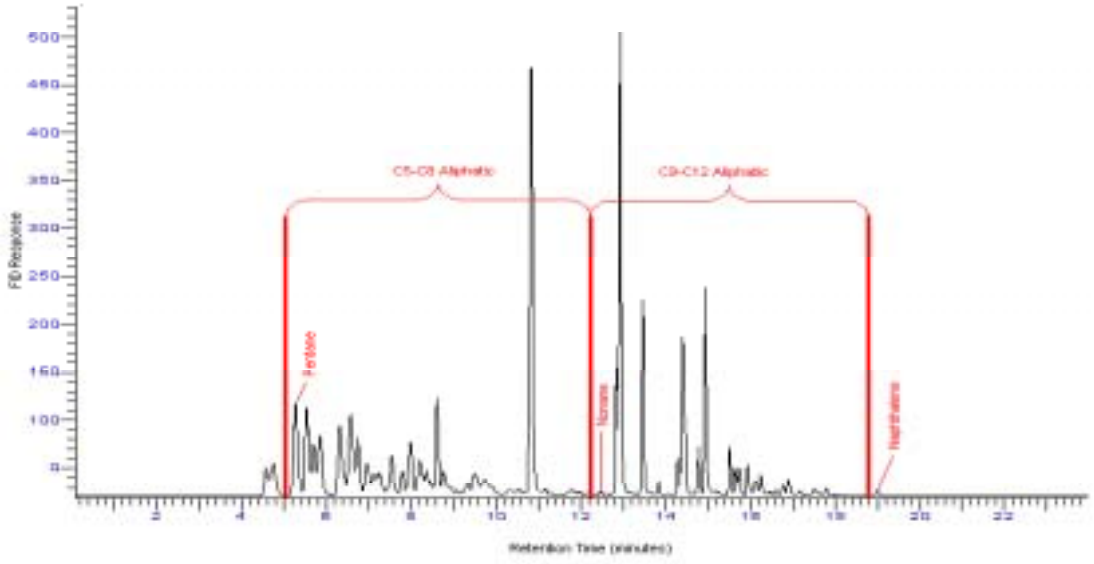


Figure 3 Gas Chromatogram (FID) of the VPH Gasoline Standard

Restek RTX-502.2 capillary column (105-m x 0.53-mm i.d., 3-μm film thickness); PID detector (10.2-eV lamp) in series with an FID detector (O.I. Analytical); Tekmar (model 3000) purge-and-trap concentrator.

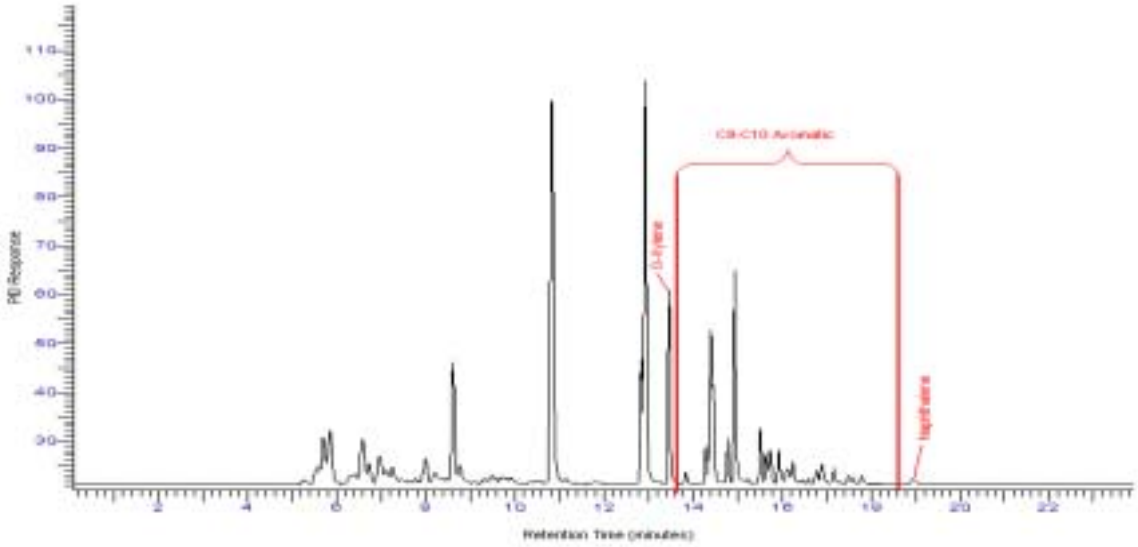


Figure 4. Gas Chromatogram (PID) of the VPH Gasoline Standard

Restek RTX-502.2 capillary column (105-m x 0.53-mm i.d., 3-μm film thickness); PID detector (10.2-eV lamp) in series with an FID detector (O.I. Analytical); Tekmar (model 3000) purge-and-trap concentrator.

APPENDIX 3

REQUIRED VPH DATA REPORT INFORMATION

APPENDIX 3: REQUIRED VPH DATA REPORT INFORMATION
Exhibit 1

SAMPLE INFORMATION

Matrix	☐ Aqueous ☐ Soil ☐ Sediment ☐ Other:		
Containers	☐ Satisfactory ☐ Broken ☐ Leaking:		
Sample Preservatives	**Aqueous (acid-preserved)**	☐ N/A ☐ pH≤2 ☐ pH>2 Comment:	
	Aqueous (TSP-preserved)	☐ N/A ☐ pH≤11 ☐ pH>11 Comment:	
	Soil or Sediment	☐ N/A ☐ Samples NOT preserved in Methanol or air-tight container	mL Methanol/g soil/sediment
		☐ Samples rec'd in Methanol: ☐ covering soil/sediment ☐ not covering soil/sediment	☐ 1:1 +/- 25%
		☐ Samples received in air-tight container:	☐ Other:
Temperature	☐ Received on Ice ☐ Received at 4ºC ± 2ºC ☐ Other: _____ ºC		

VPH ANALYTICAL RESULTS

Method for Ranges: MADEP VPH 03-1			**Client ID**				
Method for Target Analytes:			**Lab ID**				
VPH Surrogate Standards			**Date Collected**				
PID:			**Date Received**				
			Date Preserved[4]				
FID:			**Date Analyzed**				
			Dilution Factor				
			% Moisture (soil/sediment)				
Range/Target Analyte	**Elution Range**	**RL**	**Units**				
Unadjusted C5-C8 Aliphatics[1]	**N/A**						
Unadjusted C9-C12 Aliphatics[1]	**N/A**						
Benzene							
Ethylbenzene							
Methyl-tert-butylether							
Naphthalene	**N/A**						
Toluene							
m- & p- Xylenes							
o-Xylene							
C5-C8 Aliphatic Hydrocarbons[1,2]	**N/A**						
C9-C12 Aliphatic Hydrocarbons[1,3]	**N/A**						
C9-C10 Aromatic Hydrocarbons[1]	**N/A**						
PID Surrogate % Recovery							
FID Surrogate % Recovery							
Surrogate Acceptance Range				**70-130%**	**70-130%**	**70-130%**	**70-130%**

[1] Hydrocarbon Range data exclude concentrations of any surrogate(s) and/or internal standards eluting in that range
[2] C_5-C_8 Aliphatic Hydrocarbons exclude the concentration of Target Analytes eluting in that range
[3] C_9-C_{12} Aliphatic Hydrocarbons exclude concentration of Target Analytes eluting in that range AND concentration of C_9-C_{10} Aromatic Hydrocarbons
[4] Only applies to samples collected in air-tight containers.

Appendix 3 Required VPH Data Report Information
Exhibit 2

MADEP MCP Analytical Method Report Certification Form					
Laboratory Name:				Project #:	
Project Location:				MADEP RTN[1]:	
This Form provides certifications for the following data set: [list Laboratory Sample ID Number(s)]					
Sample Matrices: ☐ Groundwater ☐ Soil/Sediment ☐ Drinking Water ☐ Other: _____					
MCP SW-846 Methods Used	8260B ( )	8151A ( )	8330 ( )	6010B ( )	7470A/1A ( )
	8270C ( )	8081A ( )	VPH ( )	6020 ( )	9014M[2] ( )
As specified in MADEP Compendium of Analytical Methods. (check all that apply)	8082 ( )	8021B ( )	EPH ( )	7000 S[3] ( )	7196A ( )
	1 List Release Tracking Number (RTN), if known 2 M – SW-846 Method 9014 or MADEP Physiologically Available Cyanide (PAC) Method 3 S – SW-846 Methods 7000 Series List individual method and analyte.				
An affirmative response to questions A, B, C and D is required for "Presumptive Certainty" status					
A	Were all samples received by the laboratory in a condition consistent with that described on the Chain-of-Custody documentation for the data set?			☐ Yes ☐ No[1]	
B	Were all QA/QC procedures required for the specified analytical method(s) included in this report followed, including the requirement to note and discuss in a narrative QC data that did not meet appropriate performance standards or guidelines?			☐ Yes ☐ No[1]	
C	Does the data included in this report meet all the analytical requirements for "Presumptive Certainty", as described in Section 2.0 (a), (b), (c) and (d) of the MADEP document CAM VII A, "Quality Assurance and Quality Control Guidelines for the Acquisition and Reporting of Analytical Data"?			☐ Yes ☐ No[1]	
D	***VPH and EPH Methods only***: Was the VPH or EPH Method conducted without significant modifications (see Section 11.3 of respective Methods)			☐ Yes ☐ No[1]	
A response to questions E and F below is required for "Presumptive Certainty" status					
E	Were all analytical QC performance standards and recommendations for the specified methods achieved?			☐ Yes ☐ No[1]	
F	Were results for all analyte-list compounds/elements for the specified method(s) reported?			☐ Yes ☐ No[1]	
[1] *All Negative responses must be addressed in an attached Environmental Laboratory case narrative.*					
I, the undersigned, attest under the pains and penalties of perjury that, based upon my personal inquiry of those responsible for obtaining the information, the material contained in this analytical report is, to the best of my knowledge and belief, accurate and complete.					
Signature: _____			**Position:** _____		
Printed Name: _____			**Date:** _____		

CAM VII A, rev. 3.2 April 2004

APPENDIX 4

1. **COLLECTING AND PRESERVING VPH SOIL/SEDIMENT SAMPLES**
2. **COLLECTING AND PRESERVING VPH AQUEOUS SAMPLES**

APPENDIX 4

Collecting and Preserving VPH Soil/Sediment Samples
Page 1 of 3

OPTION 1: In-Field Methanol Preservation Technique

PERFORMANCE STANDARD: Obtain undisturbed soil/sediment sample and preserve with methanol at a ratio of 1 mL methanol per 1 gram soil/sediment.

Step 1: Choose appropriate sampling container:

60 mL wide mouth packer bottle; or
60 mL straight sided wide mouth bottle; or
60 mL VOA vial; or
40 mL VOA vial

All sampling containers should have an open-top screw cap with Teflon-coated silicone rubber septa or equivalent.

Step 2: (empty) Pre-label each container with a unique alpha/numerical designation. Obtain and record tare weight of each container to nearest 0.1 gram. *This information must be available to the laboratory performing the analyses.*

Step 3: Add 25 mLs of purge and trap grade methanol to 60 mL containers, or 15 mL to 40 mL containers. *It is essential that the methanol be purge and trap grade or equivalent quality*. Immediately cap the container. Make a mark on the 60 mL containers approximately 15 mL above the level of methanol, or a mark on the 40 mL container approximately 10 mL above the level of methanol. The objective is to obtain 25 grams of soil/sediment in the 60 mL container, or 15 grams of soil/sediment in the 40 mL container, which is approximately 15 and 10 mL of soil/sediment volume, respectively, depending upon soil/sediment type and moisture content. Other masses of soil/sediment are permissible, as long as the ratio of [grams soil/sediment]/[mL methanol] is 1:1, ±25%. Store at 4°C. *The use of a methanol trip blank prepared in this manner is recommended.*

Step 4: In the field, carefully add soil/sediment to the sample container, until the level of methanol in the vial reaches the designated volumetric mark. For wet soil/sediment, add slightly beyond the mark. IN NO CASE, HOWEVER, MAY THE LEVEL OF SOIL/SEDIMENT IN THE CONTAINER RISE ABOVE THE LEVEL OF METHANOL. The use of a 10-30 mL disposable syringe with the end cut off is recommended to obtain an undisturbed soil/sediment sample from freshly exposed soil/sediment samples. In such cases, obtain and extrude the soil/sediment into the sample container, avoiding splashing methanol out of the container.
Optional: Use a field electronic balance to ensure addition of desired mass of soil/sediment (25 grams to 60 mL containers, 15 grams to 40 mL containers).

Step 5: Use a clean brush or paper towel to remove soil/sediment particles from the threads of the sample container and screw cap. Tightly apply and secure screw cap. Gently swirl sample to break up soil/sediment aggregate, if necessary, until soil/sediment is covered with methanol. DO NOT SHAKE. Duplicate samples obtained in this manner are recommended. A split-sample must also be obtained for a determination of soil/sediment moisture content. This sample must NOT be preserved in methanol. HINT: fill this container 1/2 full, to allow screening of the sample headspace by the field investigator or the laboratory.

Step 6: Immediately place containers in cooler for storage in an upright position. Sample containers can be placed in separate zip-lock bags to protect containers in case of leakage during transport. Transport to analytical laboratory using appropriate chain-of-custody procedures and forms.

OPTION 2: Use of a Sealed-Tube Sampling/Storage Device

PERFORMANCE STANDARD: **Obtain undisturbed soil sample and immediately seal in air-tight container, for shipment to laboratory and immersion in methanol within 48 hours.**

Step 1: Obtain pre-cleaned and/or disposable samplers/containers that allow the collection and air-tight storage of at least 5-25 grams of soil.

Step 2: In the field, obtain an undisturbed sample from a freshly exposed soil. Immediately seal container, and place in a cooler. Obtain a duplicate sample to enable the determination of soil moisture content (this does not need to be in a sealed sampler/container). Transport to analytical laboratory using appropriate chain-of-custody procedures and forms.

Step 3: Samples must be extruded and immersed in purge and trap (or equivalent) grade methanol at the laboratory within 48 hours of sampling, at a ratio of 1 mL methanol to 1 gram soil. In no case, however, shall the level of soil in the laboratory container exceed the level of methanol (i.e., the soil must be completely immersed in methanol).

NOTE: Documentation MUST be provided/available on the ability of the sampler/container to provide an air-tight seal in a manner that results in no statistically significant loss of volatile hydrocarbons for at least 48 hours.

OPTION 3: Use of Alternative Collection/Storage/Preservation Techniques

PERFORMANCE STANDARD: Obtain and store an undisturbed soil sample in a manner that ensures the chemical integrity of the sample by (1) preventing the volatilization of petroleum hydrocarbons heavier than C5, and (2) preventing the biological degradation of petroleum hydrocarbons.

NOTE: The onus is on the user of such techniques to demonstrate the validity of the procedures used, via reference to published literature and/or other pertinent data.

SAFETY

Methanol is a toxic and flammable liquid, and must be handled with appropriate care. Use in a well-vented area, and avoid inhaling methanol vapors. The use of protective gloves is recommended when handling or transferring methanol. Vials of methanol should always be stored in a cooler with ice at all times, away from sources of ignition such as extreme heat or open flames.

MOST VPH/VOC AQUEOUS SAMPLES

All aqueous samples that will not be analyzed within 4 hours of collection must be preserved by pH adjustment, in order to minimize analyte losses due to biodegradation. For most samples, this can be accomplished by acidification of the sample to pH <2, by adding 3-4 drops of 1:1 HCl to a 40 mL vial. The sample should then be stored at 4°C until it is analyzed. In lieu of acidification, samples may also be preserved with an appropriate base to pH > 11.0 (see below).

SAMPLES TO BE ANALYZED FOR MTBE

ISSUE Traditionally, VPH and VOC aqueous samples have been preserved by addition of an acid (e.g., HCl) to lower the pH of the sample to less than 2.0. While this is still an acceptable approach for petroleum\hydrocarbons and most VOC analytes, recent information and data have indicated that such a technique can lead to significant losses (up to 89%) of MtBE and other ethers (White, H., Lesnik, B., Wilson, J., *Analytical Methods for Fuel Oxygenates*, LUSTLINE Bulletin #42, New England Interstate Water Pollution Control Commission, 2002 (http://www.epa.gov/swerust1/mtbe/LL42Analytical.pdf) Specifically, the combination of a low pH and high temperature sample preparation technique (e.g., heated purge and trap) hydrolyze the ether bonds present in the sample, converting the ethers into alcohols (e.g., TBA).

PRESERVATION To prevent ether hydrolysis, samples should either (a) not be acidified or (b) not be heated. Because heating the sample may be necessary to achieve proper analyte purging/partitioning, an alternative to acidification is likely to be the most efficient means to prevent hydrolysis. Because ethers are not subject to base-catalyzed hydrolysis, raising the pH of the sample is an acceptable alternative to acidification. Studies by the USEPA have shown that preservation of aqueous samples to a pH greater than 11.0 using trisodium phosphate dodecahydrate will effectively prevent biological degradation of dissolved analytes, and will not result in deleterious effects on other dissolved oxygenates or on BTEX analytes.

PROTOCOL A recommended protocol to achieve a pH level > 11.0 is to add between 0.40 and 0.44 grams of trisodium phosphate dodecahydrate to a 40 mL vial. For convenience, this can be done in the laboratory prior to sample collection in the field. Because it is more convenient to measure the required amount of trisodium phosphate dodecahydrate on a volume basis rather than by weight, the use of a pre-calibrated spoon is recommended. In the field, each vial is filled with the aqueous sample and sealed without headspace – as is traditionally done for acidified samples. The sample is then stored at 4°C until it is analyzed.

WHEN NEEDED Given the Method 1 standard for MtBE in GW-2 and GW-3 areas (i.e., 50,000 µg/L), MADEP will generally not expect or require the use of alternative preservation or analytical protocols for disposal sites located ONLY in such areas, with respect to demonstrating attainment of a condition of No Significant Risk. Nevertheless, such efforts should be considered, and may be necessary, on a case-specific basis, to investigate other site assessment objectives, such as extent of contamination, source identification, etc.

For gasoline releases in GW-1 areas, it is generally expected that some level of assessment will be conducted to confirm the concentration of MtBE using alternative preservation and/or analytical procedures to prevent hydrolysis of ethers. In particular, confirmatory samples would be recommended in the "source area" and in the outer plume (or N.D.) monitoring wells. When sampling a private or public drinking water supply well that is proximate to a release of gasoline and/or #2 fuel oil, it is generally expected that all such samples will be evaluated for the presence of MtBE by use of an alternative preservation and/or analytical procedure.

APPENDIX 5

SHIPPING METHANOL-PRESERVED SAMPLES

Shipping of Hazardous Materials

Methanol is considered a hazardous material by the US Department of Transportation (DOT) and the International Air Transport Association (IATA). Shipments of methanol between the field and the laboratory must conform to the rules established in Title 49 of the Code of Federal Regulations (49 CFR parts 171 to 179), and the most current edition of the IATA Dangerous Goods Regulations. Consult these documents or your shipping company for complete details.

Small Quantity Exemption

The volumes of methanol recommended in the VPH method fall under the small quantity exemption of 49 CFR section 173.4. To qualify for this exemption, all of the following must be met:

the maximum volume of methanol in each sample container must not exceed 30 mL
the sample container must not be full of methanol
the sample container must be securely packed and cushioned in an upright position, and be surrounded by a sorbent material capable of absorbing spills from leaks or breakage of sample containers
the package weight must not exceed 64 pounds
the volume of methanol per shipping container must not exceed 500 mL
the packaging and shipping container must be strong enough to hold up to the intended use
the package must not be opened or altered while in transit
the shipper must mark the shipping container as follows:

"This package conforms to 49 CFR 173.4"

When shipping domestically by Federal Express via ground or air, the following rules apply:

follow the inner packaging requirements of 49 CFR 173.4
no labels, placards, up arrows, or dangerous goods shipping papers are required.
if the Federal Express airbill has a shippers declaration for hazardous goods on it, check the Yes box under *Shipper's Declaration not Required.*

When shipping internationally by Federal Express, the following rules apply*:*

follow the inner packaging requirements of 49 CFR 173.4.
use dangerous goods shipping papers.
apply orientation arrows on opposite vertical sides on the exterior of the package.

Shipping Papers for International Shipments

International shipments must be accompanied by dangerous goods shipping papers that include the following:

Proper Shipping Name:	Methyl Alcohol
Hazardous Class:	Flammable Liquid
Identification Number:	UN1230
Total Quantity:	*(mL methanol/container x the number of containers)*
Emergency Response Info:	Methanol MSDS attached
Emergency Response Phone:	*provide appropriate number*
Shipping Exemption:	Dangerous Goods in Excepted Quantities

APPENDIX 6

VPH Calibration and Analysis Using Linear Regression

Use of linear regression is permissible to calculate the slope and y-intercept that best describes the linear relationship between VPH target analyte and range concentrations and instrument responses.

1. Prepare VPH Calibration Standards as described in Table 3 at a minimum of five concentration levels in accordance with the procedures and specifications contained in Section 7.0. The VPH Marker Compounds for the C_5-C_8 aliphatic, C_9-C_{12} aliphatic and C_9-C_{10} aromatic ranges are presented in Table 6.0 in Section 9.3.6.

   Analyze each VPH Calibration Standard following the procedures outlined in Section 9.5. Tabulate area responses against the concentration purged. These data are used to calculate a calibration curve for each analyte (Equation 6-1). The correlation coefficient (r) of the resultant calibration curve must be greater than or equal to 0.99.

Equation 6-1: Linear Regression: Target VPH Target Analytes

$$Area\ \ of\ \ peak = a \times concentration\ \ purged\ \left(\mu g / L\ \right) + b$$

where:

a =the calculated slope of the line
b = the calculated y intercept of the ”best fit” line

A collective calibration curve may also be established for each aliphatic and aromatic hydrocarbon range of interest. Calculate the collective calibration curve for C_5-C_8 Aliphatic Hydrocarbons and C_9-C_{12} Aliphatic Hydrocarbons using the FID chromatogram. Calculate the collective calibration curve for the C_9-C_{10} Aromatic Hydrocarbons using the PID chromatogram. Tabulate the summation of the peak areas of all components in that fraction (i.e. C_5-C_8 Aliphatic Hydrocarbons, 3 components) against the total concentration purged. These data are used to calculate a calibration curve for each VPH hydrocarbon range (Equation 6-2). The correlation coefficient (r) of the resultant calibration curve must be greater than or equal to 0.99.

Note: Do not include the area of any surrogate standard in calculating a Range calibration curve. Do not include the area of naphthalene when determining the calibration curve for C_9 - C_{10} Aromatic Hydrocarbons.

Equation 6-2: Linear Regression: VPH Aliphatic and Aromatic Hydrocarbon Ranges

$$Area\ summation\ of\ \ range\ components = a \times total\ concentration\ \ purged\ \left(\mu g / L\ \right) + b$$

where:

a = the calculated slope of the line
b = the calculated y intercept of the ”best fit” line

2. The concentration of a specific target analyte or hydrocarbon range in aqueous samples may be calculated using linear regression analysis by applying Equation 6-3.

Equation 6-3: Determination of Target VPH Analytes and Hydrocarbon Range Concentrations in Aqueous Samples using Linear Regression

$$Conc\ Analyte\ or\ HC\ Range\ (\ \mu g/L) = \left(\frac{A_x - b}{a} \right) \times D$$

where:

A_x = Response for the analyte or hydrocarbon range in the sample. Units are in area counts for Target VPH Analytes and the hydrocarbon ranges.

D = Dilution factor; if no dilution was made, D = 1, dimensionless.

a = Slope of the line for Target VPH Analyte or hydrocarbon range,

b = Intercept of the line for Target VPH Analyte or hydrocarbon range,

Note: Do not include the area of any surrogate standard in Ax when calculating a Range concentration.

3. The concentration of a specific target analyte or hydrocarbon range in a soil or sediment sample may be calculated using linear regression analysis by applying Equation 6-4.

Equation 6-4: Non-Aqueous Samples; Determination Target VPH Analytes and Hydrocarbon Range Concentrations in Soil and Sediment Samples by Linear Regression

$$Conc\ Analyte\ or\ HC\ Range\ (\mu g/kg) = \left(\frac{A_x - b}{a}\right) \times \frac{(V_t)(D)(V_w)}{(V_i)(W_d)}$$

where: A_x, a, b, and D have the same definition as for aqueous samples in Equation 6-3, and

V_t = Total volume of methanol extract, mL **(Note: this value must include the 1.0 mL surrogate spiking solution added to soil/sediment samples and the volume of water added due to % moisture correction. See Equation 12 in Section 9.6.2.2)**

V_i = Volume of methanol extract added to reagent water for purge-and-trap analysis, µL.

V_w = Volume of reagent water used for purge-and-trap analysis, µL.

W_d = Dry weight of sample, g (see Section 9.6.2.1)

Note: Do not include the area of any surrogate standard in Ax when calculating a Range concentration.

4.0 At a minimum, the working calibration curve must be verified on each working day, after every 20 samples, and at the end of the analytical sequence by the injection of a mid-level continuing calibration standard to verify instrument performance and linearity. If the percent drift for any analyte varies from the predicted response by more than ±25%, as determined using Equation 6-5, a new five-point calibration must be performed for that analyte. A greater percent drift is permissible for n-nonane. If the percent drift for n-nonane is greater than 30, note the nonconformance in the case narrative.

Equation 6-5: Percent Drift

$$\%Drift = \frac{Calculated\ concentration\ -\ Theoretical\ concentration}{Theoretical\ concentration}\ x\,100$$

APPENDIX 7

Initial Demonstration of Laboratory Capability
for the
MADEP VPH Method

1.0 Overview of the Initial Demonstration of Laboratory Capability (IDLC) Approach

2.0 Demonstration of Acceptable System Background

3.0 Initial Demonstration of Accuracy (IDA)

4.0 Initial Demonstration of Precision (IDP)

5.0 Method Detection Limit (MDL)

Table 7-1 LOQ Sample Calculation for Seven (7) System Solvent Blanks (SSBs) – VPH Ranges Only

Table 7-2 Initial Demonstration Of Laboratory Capability QC Requirements

Appendix 7
INITIAL DEMONSTRATION OF LABORATORY CAPABILITY (IDLC) for MADEP VPH Method
Page 1 of 5

For purposes of the IDLC accuracy and precision determinations (***and only this application***), the calibration mixture presented in Table 1 in Section 3.0 is considered to be representative of Volatile Petroleum Hydrocarbon (VPH) target analytes and ranges (cumulative sum of the concentrations of the range calibration standards). Other reference materials or combinations of reference materials with an individual assay for individual VPH target analytes and the C_5 through C_8 aliphatic, C_9 through C_{12} aliphatic and C_9 through C_{10} aromatic ranges are also suitable for this determination.

1.0 Overview of the Initial Demonstration of Laboratory Capability (IDLC) Approach

An IDLC must be conducted to characterize instrument and laboratory performance prior to performing analyses using the VPH Method. A laboratory may not report data to be used in support of MCP decisions unless the IDLC quality control requirements and performance standards described below and compiled in Table 7-2 are satisfied.

2.0 Demonstration of Acceptable System Background

Demonstration of Acceptable System Background is optional. To determine system background a Laboratory Method Blank (LMB) is prepared and treated exactly as a typical field sample submitted for analysis, including exposure to all glassware, equipment, solvents and reagents. A LMB for water analyses is prepared by adding 4 uL of surrogate spiking solution in purge-and-trap grade, or equivalent, Methanol to 5 mL of organic-free water (ASTM Type I reagent grade). A LMB for solid analyses is prepared by adding 100 uL of "diluted" (to obtain the same on-column nominal concentration as above) surrogate spiking solution in purge-and-trap grade, or equivalent, Methanol to 4.9 mL of organic-free water (ASTM Type I reagent grade).

At least seven (7) replicate matrix-specific LMBs should be analyzed and the mean concentration of target VPH analytes and ranges determined, as appropriate. Data produced (mean VPH target analyte and range concentrations detected related to background noise) are used to assess instrument performance of a blank sample and evaluate potential contamination from the laboratory environment, in the absence of any other analytes or system contaminants. Calculate the measured concentration of C_{mean} of the replicate values as follows.

Equation 7-1. Calculation of C_{mean} LMB

$$C_{mean} = \frac{(C_1 + C_2 + C_3 + ...C_n)}{n}$$

where,

C_{mean} = Mean recovered concentration of the replicate LMB analysis.
C_1, C_2, ...C_n = Recovered concentrations of the replicate 1,2...n.
n = at least 7

Any concentration of C_{mean} that exceeds one half of the Reporting Limit (lowest target analyte calibration or collective range calibration standard) for either a target VPH analyte or range is considered unacceptable, and indicates that a laboratory and/or LMB contamination is present. The source of the non-conformance must be identified and corrected prior to conducting any sample analysis. For purposes of acceptable system background demonstration, concentrations are determined using Equations 5 and 6 in Section 9.6 for target VPH analytes and collective ranges, respectively. Calculated concentrations below the lowest calibration standard, including zero (zero area), may be used in these calculations.

3.0 Initial Demonstration of Accuracy (IDA)

Prepare and analyze seven (7) replicate Laboratory Control Samples (LCSs) fortified at a concentration of 50% of the highest calibration curve standard (100 ug/L for waters and 5 mg/kg for soils/sediments). An LCS must be prepared and treated exactly as a typical field sample submitted for analysis, including exposure to all glassware, equipment, solvents and reagents. An LCS for water analyses is prepared by adding 4 uL of surrogate spiking solution (See Section 7.5.1) in purge-and-trap grade, or equivalent, Methanol to 5 mL of organic-free water (ASTM Type I reagent grade) An LCS for soil/sediment analyses is prepared by adding 100 uL of "diluted" (to obtain the same on-column nominal concentration as above) surrogate spiking solution in purge-and-trap grade, or equivalent, Methanol to 4.8 mL of organic-free water (ASTM

Type I reagent grade) fortified with the appropriate volume of a calibration standard or appropriate reference standard (as specified above) to obtain an equivalent concentration of 50% of the highest calibration curve standard (5 mg/ kg). Calculate the mean measured concentration (C_{mean}) of the replicate LCSs for VPH Target Analytes and ranges as follows.

Equation 7-2. Calculation of C_{mean}

$$C_{mean} = \frac{(C_1 + C_2 + C_3 + ...C_n)}{n}$$

where,

C_{mean} = Mean recovered concentration of the replicate analysis.
C_1, C_2, ...C_n = Recovered concentrations of the replicate 1,2...n.
n = 7

The value derived for C_{mean} must be within ± 30% of the true value or between 70 ug/L and 130 ug/L for waters and 3.5 mg/kg and 6.5 mg/kg for solids.

4.0 Initial Demonstration of Precision (IDP)

Using the results calculated from Section 3.0 above, calculate the percent relative standard deviation (%RSD) of the seven (7) replicate analysis, as indicated below. The %RSD must be less than or equal to 25% for both waters and solids. Higher % RSDs are allowed for n-Nonane, if included in the collective calibration standard for the C_9 through C_{12} aliphatic range. Such allowable non-conformances must be documented.

Equation 7-3. Calculation of % RSD

$$\% \text{ RSD} = \frac{S_{n-1}}{C_{mean}} \text{ X } 100$$

where,

S_{n-1}= sample standard deviation (n-1) of the replicate analyses.
C_{mean} = mean recovered concentration of the replicate analysis.

5.0 Method Detection Limit (MDL)

The determination of MDL for the MADEP VPH Method is **optional**. The reporting limit (RL) for the Method is defined as the lowest calibration standard. Determination of the lowest detectable concentration of target VPH analytes and ranges is verified on a continuing basis by analysis of the lowest concentration calibration standard and recovery of method surrogates. The recommended RL concentrations for the VPH Method do not approach (are considerably higher than) the sensitivity limits of the VPH Method for either target analytes or ranges and are more than adequate to meet the most stringent regulatory requirements of the MCP.

An MDL may be established for target VPH analytes and ranges either analytically using the 40 CFR 136 approach or by the statistical evaluation of analytical system noise as a good laboratory practice component of an overall quality control program for the VPH Method.

5.1 Determination of Method Detection Limit (MDL), 40 CFR 136, Appendix B Approach

To determine MDL values, take seven replicate aliquots of reagent water fortified at the estimated or "calculated" MDL concentration determined in Equation 7-6 below or the concentration of the lowest calibration standard, and process through the entire analytical method over a three day period. These seven MDL replicate analyses may be performed gradually over a three day period or may represent data that has been collected, at a consistent MDL "calculated" concentration, over a

series of more than three days. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

Equation 7-4. Calculation of MDL based on Laboratory Analysis

$$MDL = (t_{n-1}) \times (S_{n-1})$$

where,

t_{n-1} = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t_{n-1} = 3.14 for seven replicates]
S_{n-1} = Sample standard deviation (n-1) of 7 replicate MDL analyses (equivalent to a "low-level" LCS)

5.2 Determination of Method Detection Limit (MDL) and Limit of Quantitation (LOQ) by Statistical Evaluation of System Noise

Seven (7) replicate aliquots of a System Solvent Blank (SSB) must be prepared and analyzed exactly as a typical field sample submitted for analysis, including exposure to all glassware, equipment, solvents and reagents. A SSB for water analyses is prepared by adding 4 uL of purge-and-trap grade or equivalent, Methanol to 5 mL of organic-free water (ASTM Type I reagent grade). A SSB for soil/sediment analyses is prepared by adding 100 uL purge-and-trap grade, or equivalent Methanol to 4.9 mL of organic-free water (ASTM Type I reagent grade).

Data produced are used to assess the level of noise and the baseline rise attributable solely to the GC system, in the absence of any other analytes or system contaminants. These data are used to calculate the Limit of Quantitation (LOQ) and Method Detection Limit (MDL) using the Keith statistical approach. ***For these analyses, the data system's threshold for peak area integration must be adjusted to ensure that a positive value is recorded for the target VPH analytes and ranges of interest, as practical. Tabulate the area responses for each target VPH analyte and range. Calculate the LOQ and MDL using Equations 7-5 and 7-6, respectively. An example LOQ and MDL calculation for the VPH aliphatic and aromatic ranges for an aqueous sample is presented below in Table 7-1.***

Equation 7-5. Calculation of Limit of Quantitation (LOQ)

$$LOQ_x = 10 * S_{x,n-1} CF_x$$

$S_{x,n-1}$ = Sample standard deviations for peak areas of VPH target analytes and ranges of interest for the seven (7) replicate System Solvent Blanks (SSBs) reported in appropriate units.
CF_x = Representative Calibration Factor for appropriate VPH Target analyte or Range

Equation 7-6. Calculation of MDL

$$MDL = LOQ/3$$

Table 7-1 LOQ Sample Calculation for Seven (7) System Solvent Blanks (SSBs) – VPH Ranges Only

Replicate Number	VPH Range (Area Units)		
	C_5 - C_8 aliphatic	**C_9 - C_{12} aliphatic**	**C_9 - C_{10} aromatic**
1	32887	41407	18427
2	54035	26628	18294
3	10991	38536	17885
4	19382	12497	20846
5	9730	32572	14570
6	37624	11564	18709
7	87050	15501	16545
Range Average	24765	25529	17892
Calculations:			
Range $S_{x, n-1}$	15994	11573	1801
Range CF (ug/L * AU^{-1})	0.00010	0.00007	0.00003
LOQ (ug/L)	16	8.1	0.5
MDL (ug/L)	5.3	2.7	0.17

Table 7-2 Initial Demonstration Of Laboratory Capability QC Requirements

Reference Section	Requirement	Specification & Frequency	Acceptance Criteria
2.0	Initial Demonstration of Acceptable System Background (Optional)	Analyze at least 7 replicate Laboratory Method Blanks (LMB) fortified with surrogate spiking solution. Calculate the mean recovered concentration for each Target VPH analyte and hydrocarbon range. See Equation 7-1 in Section 2.0.	The mean LMB concentrations must be <½ of the RL (lowest point on calibration curve or lowest cumulative range calibration standard).
3.0	Initial Demonstration of Accuracy (IDA)	Analyze 7 replicate LMBs fortified with VPH calibration standards at a nominal concentration of 100 ug/L or 5 mg/kg for each standard analyte. Calculate the mean recovered concentration (C_{mean}) for each target VPH analyte and hydrocarbon range. See Equation 7-2 in Section 3.0.	The C_{mean} must be ± 30% of the true value of the aliphatic and aromatic ranges and target analytes for both waters and soils.
4.0	Initial Demonstration of Precision (IDP)	Calculate percent relative standard deviation (%RSD) of IDA replicates for each target VPH analyte and hydrocarbon range. See Equation 7-3 in Section 4.0.	The %RSD must be ± 25% for both waters and solids
5.0	Method Detection Limit (MDL) Determination (Optional)	Select a fortifying level at the estimated or "calculated" MDL or RL for the LCS. See Equation 7-6 in Section 5.2. Analyze these 7 replicate "low-level" LCSs over multiple days and calculate MDL using Equation 7-4 in Section 5.1. Do not subtract any blank contribution to this value. MDL may also be determined by a statistical evaluation of system noise based on the analysis of seven (7) system solvent blanks (SSB). See Section 5.2	See 40 CFR 136, Appendix B The MDL must be < ½ of the RL for individual target VPH analytes and < ½ or the RL for collective VPH hydrocarbon ranges (See Section 12.0).

Continuing QC for each Analytical Batch (up to 20 samples of a similar matrix analyzed contemporaneously)

QC Element

Opening mid-range continuing calibration standard (O-CCS)
Closing mid-range continuing calibration standard (C-CCS)
Laboratory Method Blank (LMB)
Full Analyte Laboratory Control Sample (LCS)
Full Analyte Laboratory Control Sample Duplicate (LCSD)